CHAPTER III

Liquid crystal dimers Non symmetric azo - based liquid crystal dimers
III. 1. Introduction

A liquid crystal (LC) dimer is formed by covalently linking two mesogenic segments through a flexible spacer. The vast majority of low molar mass molecules forming LC phases are composed of relatively rigid aromatic or aliphatic rings with alkyl chains attached to one or both the ends. In essence, it is the anisotropic interactions between the rigid cores and flexible alkyl chains that lead to the formation of LC phases. In this respect LC dimers represent an inversion of the conventional molecular design for low molar mass mesogens as they contravened the accepted structure-property relationships by consisting of molecules having a highly flexible central unit rather than a semi-rigid cyclic core [1]. Several names such as dimesogens, bimesogens, twins etc., have been used to refer to these materials though the most preferred nomenclature is dimers. Initial interest in these LCs stemmed from their ability to act as model compounds for semi-flexible main chain liquid crystal polymers [2]. These polymers are not only of interest for their application potential but also for unusual liquid crystalline behaviour such as the dependence of their transitional properties on the length and parity of the flexible spacers, the occurrence of alternating smectic phases etc [3]. However, the interpretation of the LC behaviour of these polymers by theoretical and experimental investigations is complicated due to their inherent molecular structural heterogeneity. Griffin and Britt argued that in semi flexible main chain liquid crystal polymers the fundamental repeating unit contains two mesogenic units linked by a flexible spacer and hence an alternative approach to study these polymers through the investigations on mono dispersive dimers [2]. They proved the dependence of thermal behaviour on the length and parity of the flexible
spacer in a low molar mass LC dimer, reminiscent to that observed in polymeric systems. Then it became quickly apparent that the dimers are of significant interest in their own right as they display different mesomorphic behaviour to conventional LCs [1-5]. LC dimers are the lowest possible oligomers exhibiting characteristic properties such as thermal behaviour, glass transitions etc., of polymers while still retaining the fluidity, viscosity etc., of low molar mass LCs and hence are promising systems for many practical applications [6]. In Fig.III.1 we present a general template that describes the structure of liquid crystal dimer. As mentioned earlier, they are usually composed of molecules containing two conventional mesogenic groups linked by a flexible spacer. A and B represent mesogenic core units consisting of linearly linked aromatic or alicyclic rings that sometimes consist of hetero atoms. X and Z are linking groups that attach the terminal R and R' moieties (which in most cases are moderately long flexible units such as alkyl or alkoxy chains or some polar groups like cyano or nitro) to the mesogenic core. M and N are lateral substituents on the mesogenic core that are not present for all systems. Most of the LC dimers contain flexible alkylene spacers. The central flexible spacer together with the mesogenic core structures A and B form the ‘rigid core’ of the dimeric molecule.

Figure III. 1: A general structural template for liquid crystal dimer
LC dimers can be broadly classified into two categories; symmetric and non-symmetric. In the former class of dimers the molecular structures of mesogenic entities are identical whereas in the latter case they are different. These two groups can be further sub-divided according to the molecular shape geometry of the two mesogenic entities. Some of the examples are symmetric calamitic dimers (I) [7], nonsymmetric calamitic dimers (II) [8], symmetric discotic dimers (III) [9], nonsymmetric discotic-calamitic Dimmers (IV) [10], supramolecular non-symmetric dimers (V) [11] etc (see Fig.III.2).

**III. 1. 1. **Structure-property relationship in liquid crystal dimers

The extensive study on the LC dimers with different molecular architectures have revealed their dependence of mesomorphic behaviour on the various molecular structural factors and are briefly discussed under the following headings.

(a) **Molecular structure of the mesogenic entities**

The vast majority of liquid crystal dimers reported in the literature consist of two identical rod-like mesogenic units linked in terminal positions via a spacer and the dependence of the transitional properties on the structure of the mesogenic group parallels that observed for conventional low molar mesogens [11, 12]. For example, increasing the length of the core by inserting short unsaturated linkages...
between phenyl rings enhances the clearing temperature while lateral substitutions on the core causes the clearing temperature to fall. The most extensively studied series of symmetric dimers, the \( \alpha, \omega \)-bis (4’-cyanobiphenyl-4-yl oxy)alkanes (I) exhibit only the nematic phase [8]. These are considered as the dimeric analogues of 4-n-alkyloxy-4’-cyanobiphenyls which are amongst the most widely studied series of conventional low molar mass LCs. On the other hand, the smectic tendencies in the symmetric dimers were observed in \( \alpha, \omega \)-bis [4-(4-alkylphenyliminomethyl) phenoxy] alkanes (VII) and they are considered as the dimeric analogues of N-(4-n-alkyloxybenzylidine)-4’-n-alkylanilines (VIII) [12].

The most common terminal groups used are either the alkyl or alkoxy chains. The effects of a range of terminal substituents on the clearing temperatures of symmetrical dimers are similar to those observed for conventional LCs. For example, Jin et al. established the efficiency of the terminal group in enhancing the nematic behaviour for the dimer series (IX) to be of the order as shown below [13]. This behaviour is in good agreement with the conventional low molar mass nematogens.

\[
X = -H < -\text{CH}_3 < -\text{Cl} < -\text{NO}_2 = -\text{CHO} < -\text{CN} < -\text{C}_6\text{H}_5
\]

Many series of non-symmetrical dimers have been characterized and this has resulted in the discovery of a novel family of smectic phases. In the majority of cases the differing mesogenic cores have been chosen so that they exhibit a specific molecular interaction. Examples under this category include, connecting
an electron deficient moiety with an electron rich segment \( \text{(II)} \) in order to make way for specific molecular interactions [14]. Two mesogenic entities can be attached by covalent bonds or via intermolecular hydrogen bonding interaction between suitable hydrogen bond donors and acceptors \( \text{(V)} \). In the case of dimers with a photo responsive moiety such azobenzene induce photochemical phase transitions based on its \textit{cis-trans} isomerizations [5]. Bae \textit{et al.} investigated the effects of changing the relative position of attachment of spacers to the mesogenic units on liquid crystal behaviour [15]. The three possible structures are the conventional linear dimer \( \text{(X)} \), an H-shaped dimer \( \text{(XI)} \) in which the mesogenic units are laterally attached and a T-shaped dimer \( \text{(XII)} \) containing a terminal and a laterally linked mesogenic units. The linear dimers exhibit the highest clearing temperatures and the lateral dimers the lowest. Smectic behaviour was observed only for the lateral dimers while the linear and T-shaped dimers exhibit solely the nematic behaviour.
The length, parity and chemical nature of the flexible spacer

The length, parity and chemical nature of the central spacer have been shown to have an important influence on the thermal properties of the system. The most general manifestation of this spacer effect is the alternation in the clearing temperatures and in the enthalpy and entropy changes associated with the phase transitions observed on varying the number of carbon atoms in the spacer. In the nematogenic series (I), a pronounced odd-even effect is apparent in which the even members of the series exhibit the higher values of clearing temperatures although this alternation is attenuated on increasing the number of methylene units [6]. For the majority of the symmetric dimers containing terminal alkyl chains a simple empirical rule has emerged relating the molecular structure to the occurrence of the smectic behaviour; specifically, "if a symmetric dimer is to exhibit a smectic phase then the terminal chain length must be greater than half the spacer length". X-ray diffraction study on such compounds showed that the molecules are arranged in monolayers in the smectic phases [12]. Later, it was found that in systems where the terminal chain and spacer lengths are compatible, an intercalated SmA phase was formed. It is considered that the intercalated smectic phase formation is driven by an increase in entropy as a result of homogeneous mixing of the mesogenic groups, rather than their segregation into different spatial regions as in the case of monolayer arrangement. Also for the non-symmetric dimers depending on the various molecular constraints, monolayer, intercalated and interdigitated smectic phases are stabilized.

Most of the LC dimers contain flexible alkylene spacers and only a few dimers contain chemically different spacers such as the oligooxyethylene (XIII)
[16] or siloxane (XIV) [17] chains. Creed et al. [16a] showed that a disiloxane spacer would reduce the transition temperatures compared to an alkylene spacer because of its higher flexibility. Both Jo et al. [17b] and Aquilera and Bernal [17c] have noted the strong tendency of disiloxane linked dimers to exhibit smectic rather than nematic behaviour.

Not only does the chemical nature of the spacer but also the type of link between the spacer and the mesogenic entity affect the transitional properties of the dimers. Jin and co-workers [18, 19] showed that exchanging ether linkage by an ester group in the dimeric series tends to promote smectic behaviour which is believed to be a consequence of the enhanced lateral interactions arising from the contribution of the dipole on the carbonyl group. Ferrarini et al. [19] and Abe et al., [20] attribute such a phenomenon to the total molecular geometry of the dimers.
The presence of chiral groups

It is well documented that the molecular chirality greatly influences the mesomorphic behaviour of conventional LCs. The dimers comprising of chiral entity have been no exception to the influence of molecular chirality on the mesomorphism. In dimers, the molecular chirality can be introduced through a chiral mesogenic core, chiral terminal tail, or chiral spacer. An interesting investigation on LC dimers has been the evaluation of the effect of the spacer parity on the transitional properties and the form chirality of the phase. Blatch et al. [21] studied the symmetric (XV) and nonsymmetric (XVI) Schiffs base chiral dimers and found that it indeed exhibits an odd even effect in the transition temperatures but with no such effect on the helical twisting powers. Nishiyama et al. have reported the synthesis and properties of chiral symmetric dimers that display ferroelectric and antiferroelectric phases with high values of tilt angle [22].

Jin et al. [23] were the first to employ cholesteryl ester moiety as the chiral entity to form chiral non-symmetric dimers (XVII) which found to exhibit a rich polymorphic sequence including an incommensurate smectic A (SmAic) phase. Tamaoki et al. have reported several low molar mass dicholesteryl esters (for
example compound XVIII) exhibiting N* phase to fix selectively the pitch in the
glassy state to have potential use in rewritable colour recording [24].

Molecular architecture of liquid crystal dimers with two mesogenic groups linked
via a flexible spacer allows enormous structural variations for realizing various
LC materials. The examples given here highlight the complex interplay of the
different segments in the mesophase formation of liquid crystalline dimers and the
need for the synthesis of new compounds in order to establish generalized
structure property relationships.

III. 2. Non-symmetric azo-based liquid crystal dimers

III. 2. 1. Scope of the work

Non-symmetric liquid crystal dimers are composed of molecules possessing two
non-identical anisomeric units linked through a flexible spacer. From the past one
decade, dimeric liquid crystals have attracted much attention as they are found to
exhibit new liquid crystalline phases [3], serve as useful models for semi-flexible
main chain liquid crystalline polymers [2] and show unique properties applicable
for optical materials [5]. As mentioned earlier, one of the most extensively studied
series of dimers are α,ω-bis(4’-cyanobiphenyl-4-yloxy)alkanes (I) that are
reported to show only the nematic phase even though the analogous conventional
monomers show smectic behaviour [6]. This observation has been attributed to the
increased molecular flexibility of the dimer. The nematic to isotropic transition temperatures (TN-I) and the associated entropy changes were critically dependent on the length and parity of the spacer and the terminal alkoxy chain. Specifically a large odd-even effect was apparent in which the even members of the series exhibit the higher values of TN-I although the alternation is attenuated on increasing the length of the spacer.

The vast majority of liquid crystal dimers reported in the literature consist of two identical rod-like mesogenic units linked in terminal positions via a flexible alkyl chain normally containing between 3 and 12 methylene units; the behaviour of such materials has been recently reviewed [25,26]. Ferrarini et al theoretically predicted the nature of the link between the spacer and the mesogenic units to determine the transitional properties of liquid crystal dimers [27]. In order to test these predictions a wide range of dimers have been prepared containing either ether or methylene linking groups [28, 29, 30]. The dimers in which two mesogenic units differ are referred to as non-symmetric dimers. For this series the nature of the SmA phase depends on the relative lengths of the spacer and terminal chains, in which for short terminal chains the intercalated smectic A phase is formed. While for long terminal chains an interdigitated smectic A phase is observed. It has been suggested that a specific dipolar interaction may exist between the ester groups of the spacer and the ether groups of the terminal chains to stabilize the intercalated structure. The strong dependence of the phase type on the parity of the spacer has been interpreted in terms of molecular shape and ease at which the more linear even members are accommodated within the intercalated
SmA phase. By comparison an odd spacer dimer packs more efficiently into the intercalated SmC phase.

Liquid crystal dimers can act as the models for main group liquid crystalline polymers that allow the study of the flexibility and properties of different mesogenic groups. The dimeric liquid crystals retain the crucial structural components of many thermotropic group polymers, namely a flexible spacer linking two mesogenic groups are easier to study and are amenable to direct interpretation [29-31]. It is the anisotropic interaction between cores and the alkyl chains that gives rise to liquid crystalline phases [11]. In recent years the studies are also focused on the molecular engineering and synthesis of intermediate molecular architectures called supermolecular LCs (oligomesogens), this is because oligomesogens offer a practical means of introducing desirable and different functionalities through the combination of appropriate functional mesogenic segment [32-41]. The thermal behavior of dimers containing alkyl spacers is quite different from that of the conventional low molar mass.

The azobenzene derivatives are very effective for controlling liquid crystals by light because the geometrical change by photo isomerization could yield a concomitant change in chemical and physical properties not only in the azobenzene itself but also in the macro environments around it. Such photonic control has been mainly applied in a nematic (N) phase by means of transmission, reflection and light scattering mode. Photoresponsive properties of azobenzene derivatives by means of photoisomerization are already reported [42-50].

It is reported that an addition of chromophores, such as azo groups are found the lower required in optical field [51]. The photo induced birefringence has
extremely high and long term stability and holograms recorded shown no
degradation. This feature has made the photo chromic materials in particular the
azo compounds are very promising candidates for optical data storage. Several
groups have done extensive work in this field [52-59]. The present investigation
has been undertaken with an emphasis to provide thermal stability and to
understand the molecular structure-property in relationship with azo based
unsymmetrical dimers. These novel compounds consist of azo benzene unit
connected to alkyloxy benzoyloxy phenol through either odd or even alkylene
spacers.

**III. 2. 2. Molecular design**

To understand the underlying relation between molecular structure and the
phase behaviour in dimers, we propose to study a new series of symmetric dimers
consisting of 4-ω-bromo alkyloxy-4-butylazobenzene and 4-(4-alkyloxy
benzoyloxy) phenol cores connected through either odd or even flexible alkylene
spacer via ether linkages. Two series of unsymmetrical dimers have been realized.
In the following section we present the synthesis and characterisation of the
compounds in detail. A general molecular structure of the target dimer is shown
below.

\[
\text{C}_4\text{H}_9-N=N-O(\text{CH}_2)_mO-\text{O-Carbonyl-O-C}_{n+1}\text{H}_{2n+1}
\]

\[
m = 7 \text{ and } 8
\]

\[
n = 3 \text{ to } 11
\]
III. 2. 3. Synthesis and molecular structural characterization

The non symmetric dimers and their intermediates (1b and 2c) were realized as outlined in Scheme A-n and scheme B-n. Firstly, 4-butyl aniline was diazotized using hydrochloric acid, sodium nitrite; sodium hydroxide and sodium carbonate provide the compound (1a). Alkylation of this compound with α,ω-dibromoalkane give the intermediate (1c). The hydroxyl intermediate (2c) were synthesized in three steps starting from 4-hydroxy benzoic acid, it was first subjected to O-alkylation with n-bromo alkanes in the presence of KOH as a strong base in refluxing diethylene glycol to obtain compound (2a). The esterification of this material with 4-benzylxy phenol, dicyclohexylcarbodiimide, N, N-dimethylaminopyridine and dichloromethane as the solvent to obtain compound (2b). Reduction of this compound by 10% Pd/C using ethyl acetate as the solvent gives the intermediate (2c). Azo benzene was condensed with various (alkyloxybenzoyloxy) phenol under basic reaction condition in dimethyl formamide to obtain the target dimers in reasonably good yield. The molecular structures of all the compounds were confirmed by spectroscopic analysis (see experimental section). As a representative case the $^1$H and $^{13}$C NMR spectra of the dimer is shown in Fig.III.3 and Fig.III. 4

![Figure III. 3. $^1$H NMR (400MHz) spectra of A-10 in CDCl₃](image)
Figure III. 4. $^{13}$C NMR (100MHz) spectra of A-10 in CDCl$_3$. 
**Scheme A-n**  
X=8, n = 3, 4, 5, 6, 7, 8, 9, 10, 11

**Scheme B-n**  
X=7, n = 3, 4, 5, 6, 7, 8, 9, 10, 11

**Reagents and condition:**  
(i) sodium nitrite, HCl, 0-2 °C;  
(ii) phenol, aq.NaOH, Na₂CO₃, 0-2 °C;  
(iii) dibromoalkanes, anhyd K₂CO₃, acetone reflux 18 h;  
(iv) monobromoalkanes, anhyd.KOH, diethylene glycol, reflux, 18 h;  
(v) benzylxyphenol, DCC, DMAP, dichloromethane; (vi) 10% pd/C, ethylacetate;  
(vii) anhyd K₂CO₃, KI (catalytic), Dimethylformamide, reflux, 20 h
III. 2. 4. Results and discussions

The identification of the mesophases and determination of phase transition temperatures were achieved with the help of polarizing optical microscope (POM). The sample placed between a clean untreated glass slide and a cover slip was used for this particular study. The mesophase assignment was based on the observation of birefringence and fluidity when examined under POM. To confirm the transition temperatures and to determine their associated enthalpies, a differential scanning calorimeter (DSC) calibrated using pure Indium was employed. The peaks observed in DSC traces (obtained at a rate of 10°C/min.) due to phase transition was reproducible and peak temperatures were consistent with those deduced from the optical experiments.

In an effort to understand the structure-property relations the chain lengths of both the paraffinic spacer (within limits) as well as of terminal alkoxy tails of ester moiety have been varied. The thermal behaviour and phase transition temperatures of the dimeric compounds of scheme A-n and scheme B-n are summarized in table 1 and table 2. It is clear from table 1 and table 2 that all the dimers exhibit enantiotropic mesomorphism, especially the nematic (N) behaviour. The observation of POM of A-7, it has Cr-Cr transition after the display of nematic phase on heating; the enthalpy could not be measured on cooling due to the onset of crystallization, it display enantiotropic smectic A (plate III.2.4.1), smectic C (plate III.2.4.2) and nematic phases (plate III.2.4.3). Notably; in scheme B-n, the dimer B-4 with heptyl methylene spacer and in scheme A-n, the dimer A-6 with octa methylene spacer displays unknown mesophase smectic X (plate III.2.4.4) which is meta stable in nature.
Plate III. 2. 4. 1 Polarising optical microscope textures of SmA focal conic at 101.2°C exhibited by the compound A-7.

Plate III. 2. 4. 2 Polarising optical microscope texture of SmC schlieren at 81.2°C exhibited by the compound A-7.
Plate III. 2. 4. 3 (a) Polarising optical microscope textures of Nematic schlieren at 135. 3°C exhibited by the compound A-7.

Plate III. 2. 4. 4 Polarising optical microscope texture of SmX at 102. 3°C mesophase exhibited by the compound B-4.
It is shown from table 1 that the lower homologues A-3 and A-4 exhibit enantiotropic nematic phase. A-5 to A-11 show smectic C mesophase except A-9, which display only nematic phase. On cooling the isotropic liquid of any homologue placed between a pair of clean glass slides, nematic phase appears with droplets emanating from the dark background. Within the droplets curved dark brushes (schlieren pattern) with director fluctuations occur.

On cooling further, the nematic droplets coalesce to give classical schlieren texture of high birefringence with both two brush and four brush as a representative case of all the compounds in series A-n and series B-n. On further cooling, the schlieren texture transforms to a threaded pattern. The texture flashed when subjected to mechanical stress.
Table 1: Phase transitions temperatures (°C) and the corresponding enthalpies (J/g) of liquid crystalline dimers of heptyl spacer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Cr Heating Cooling</th>
<th>SmX Heating Cooling</th>
<th>SmC Heating Cooling</th>
<th>SmA Heating Cooling</th>
<th>N Heating Cooling</th>
<th>I Heating Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-3</td>
<td>3</td>
<td>81.2[39.2] 68.4[23.3]</td>
<td>- -</td>
<td>• 104.2[1.2] 107.2[2.1]</td>
<td>• 82.1[0.8] 78.0[0.4]</td>
<td>• 166.6[1.6] 164.8[1.5]</td>
<td></td>
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<tr>
<td>B-4</td>
<td>4</td>
<td>93.6[39.9] 65.4[30.1]</td>
<td>• 103.6[0.4] 102.3[0.3]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
<td>130.6[0.4] 129.9[0.3]</td>
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<tr>
<td>B-5</td>
<td>5</td>
<td>81.1[76.4] 61.6[52.4]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>B-7</td>
<td>7</td>
<td>111.9[71.9] 88.3[27.4]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-8</td>
<td>8</td>
<td>67.9[47.0] 52.5[13.4]</td>
<td>- -</td>
<td>• 98.8[6.6] 99.2[6.1]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-9</td>
<td>9</td>
<td>101.7[51.5] 69.9[9.1]</td>
<td>- -</td>
<td>• 97.2* 94.1[25.1]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-11</td>
<td>11</td>
<td>50.4[14.6] 39.1*</td>
<td>- -</td>
<td>• 76.8[0.1] 72.9[1.3]</td>
<td>- -</td>
<td>-</td>
<td>-</td>
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</table>

*Onset of crystallization; Cr-Crystal; SmC- Smectic C; SmA- Smectic A; N- nematic; I- Isotropic
Subsequent increases in the length of the terminal chains cause the clearing temperature to fall except A-3 and A-8 which has the highest clearing temperature of 179.1°C and 171.1°C. In the heating as well as cooling scans the compounds with even methylene spacer (eight), the higher homologue nine exhibit only nematic phase when compare to the lower homologue A-6, A-7 and A-8. Smectic C phase was emerged for B-3, B-6, B-8, B-9, B-10 and the higher terminal alkoxy chain B-11. For the odd metylene spacer smectic A phase was display for the terminal alkoxy chains three and four, the longer chains has not display smectic A phase. Results of the thermal transitions and texture analysis exhibit schlieren textures of the smectic C phase and dark field smectic A phases. As the methylene spacer increases from seven to eight the clearing temperature became high.

Upon DSC analysis the non symmetrical dimer A-6 exhibited typical transition behaviour. Four enantiotropic transitions, isotropic to nematic, nematic to smectic C, smectic C to smectic X and smectic X to crystal were observed. The clearing temperature decreased with increase the length of side alkoxy chain. The clearing temperature for the even membered spacer is considerably higher than those for the odd membered spacer. As a representative case the DSC scans obtained at a rate of 10°C/min for the A-6 sample are shown in Fig.III.5
Table 2: Phase transitions temperatures (°C) and the corresponding enthalpies (J/g) of liquid crystalline dimers of octyl spacer.

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Cr</th>
<th>Heating Cooling</th>
<th>SmX Heating Cooling</th>
<th>SmC Heating Cooling</th>
<th>SmA Heating Cooling</th>
<th>N Heating Cooling</th>
<th>I</th>
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<tr>
<td>A-3</td>
<td>3</td>
<td>•</td>
<td>134.9[25.9]</td>
<td>104.2[1.2]</td>
<td>-</td>
<td>176.0[7.4]</td>
<td>164.0[8.6]</td>
<td>•</td>
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<tr>
<td>A-4</td>
<td>4</td>
<td>•</td>
<td>98.6[72.8]</td>
<td>103.6[0.4]</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>67.3[19.1]</td>
<td>102.3[0.3]</td>
<td></td>
<td></td>
<td></td>
<td>164.0[8.6]</td>
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<tr>
<td>A-5</td>
<td>5</td>
<td>•</td>
<td>93.8[33.1]</td>
<td>81.2[8.8]</td>
<td>-</td>
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<td></td>
<td></td>
<td>71.1*</td>
<td></td>
<td>79.1[1.2]</td>
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<td>158.9[3.5]</td>
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<tr>
<td>A-6</td>
<td>6</td>
<td>•</td>
<td>69.9[53.5]</td>
<td>112.7[0.7]</td>
<td>-</td>
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<td>-</td>
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<td></td>
<td></td>
<td>74.3[3.8]</td>
<td>111.5[0.9]</td>
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<td></td>
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<td>148.1[2.2]</td>
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<tr>
<td>A-7</td>
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<td>•</td>
<td>61.9[52.5]</td>
<td>80.8[2.7]</td>
<td>-</td>
<td>99.8[1.9]</td>
<td>-</td>
<td>•</td>
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<tr>
<td></td>
<td></td>
<td>48.5*</td>
<td></td>
<td>81.2[1.6]</td>
<td></td>
<td>101.2[1.6]</td>
<td>136.9[1.5]</td>
<td></td>
</tr>
<tr>
<td>A-8</td>
<td>8</td>
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<td>57.6[5.6]</td>
<td>104.4[42.7]</td>
<td>-</td>
<td>135.7[1.1]</td>
<td>172.1[5.5]</td>
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<td></td>
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<td>48.2*</td>
<td></td>
<td>101.9[12.2]</td>
<td></td>
<td>133.4[0.7]</td>
<td>171.1[5.0]</td>
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<tr>
<td>A-9</td>
<td>9</td>
<td>•</td>
<td>101.5[71.8]</td>
<td>80.8[2.7]</td>
<td>-</td>
<td>133.5[2.5]</td>
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<tr>
<td>A-10</td>
<td>10</td>
<td>•</td>
<td>101.7[51.5]</td>
<td>92.8*</td>
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<td>69.9[9.1]</td>
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<td>122.2[1.3]</td>
<td></td>
</tr>
<tr>
<td>A-11</td>
<td>11</td>
<td>•</td>
<td>60.4[19.8]</td>
<td>74.6[8.8]</td>
<td>-</td>
<td>81.0[12.1]</td>
<td>-</td>
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<tr>
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<td>52.1[2.9]</td>
<td>68.3[13.9]</td>
<td></td>
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<td>81.0[12.4]</td>
<td>110.7[6.7]</td>
<td></td>
</tr>
</tbody>
</table>

*Onset of crystallization; Cr-Crystal; SmX- Smectic X; SmC- Smectic C; SmA- Smectic A; N- nematic; I- Isotropic
Figure. III. 5. Differential scanning calorimetric thermogram of compound A-6 obtained at a rate of 5°C min⁻¹: (a) heating cycle (b) cooling cycle.

All the compounds show phase sequence I – N – Cr. Subsequent increase in the length of the terminal chains cause the clearing temperature to fall, showing initially an alternation which attenuates and the stability of smectic phases increases with increasing the side chain in case of odd membered (heptyl)spacer. It is not apparent why the addition of a single methyl group should have such a profound effect on transition temperatures although it has been suggested that this results from a change in the shape of the mesogenic group rather than from its anisotropy. The phase stabilities of the azo dimers are attributed to a difference in angle between the planes of the benzene rings influenced by the linking group. For the azo linkage, the benzene rings are planar.

III. 2. 5. Conclusion

We synthesized homologous azo-typed dimers consisting of an azo benzene mesogenic units with terminal alkoxy chains (n=3 to 11) and methylene units 7 and 8. The compound of n=6 (even spacer) and n=4 (odd spacer) showed enantiotropic SmX phase. Combining the results of odd and even methylene spacer, even spacer exhibit SmA phase with increasing terminal alkoxy chain while the lower homologous of odd spacer shows SmA phase.
III.2.6. Experimental

In this section the detailed synthetic procedures and the molecular structural characterization data has been presented for the intermediates and target compounds of scheme A-n and scheme B-n.

General procedure for the synthesis of 4-hydroxy-4-butylazo benzene (1a)

An aqueous solution of NaNO$_2$ (1.0equiv.) was added dropwise to a well stirred and pre cooled solution of 4-butyl aniline (1.0equiv.) in mixture of 10ml of water and 15 ml Con.HCl. The resulting diazonium solution was quenched with a solution of Phenol (1.0equiv.) in NaOH (1.3g) and Na$_2$CO$_3$ (4g) in 25ml of water at 0-2°C. The reaction mixture was allowed to warm up to room temperature and stirred for 10 hours. An orange coloured solid precipitated out which was filtered on a buchner funnel. The air-dried sample was further purified by repeated recrystallization from aqueous EtOH to obtain products in reasonably good yield (79%).

1a: $R_f = 0.4$ in 30% EtOAc-hexane; A yellow solid; m.p.81°C; IR (KBr pellet): 3432, 2857, 1652, 1025 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 7.70-7.62 (m, 2H, Ar), 7.28-7.24 (m, 4H, Ar), 2.69 (t, 2H, Ar), 2.66 (t, 2H, 1XCH$_2$), 1.71-1.56 (t, 2H, 1XCH$_2$), 1.47 (m, 2H, 1XCH$_2$), 0.95 (t, 3H, 1X CH$_3$).

General procedure for the synthesis of 4-ω-bromo alkyloxy-4-butylazobenzene (1b or 1c)

A 100ml flask equipped with water condenser and nitrogen inlet, was charged with acetone (50ml), anhydrous K$_2$CO$_3$ (4.0equiv.), 4-hydroxy-4-butylazo benzene (1a) (1.0equiv.), and 1, n-dibromoalkane (6.0equiv.), and then flushed with nitrogen for some time. After closing the neck with a septum, the reaction
mixture was refluxed for 16 hours with vigorous stirring and filtered hot through a celite bed. The filtrate was evaporated and the crude mass obtained was dissolved in CH₂Cl₂, washed with brine, and dried over Na₂SO₄. Evaporation of solvent gave a yellow solid, which was purified by column chromatography using silica gel (100-200 mesh). Elution with a mixture of 5% EtOAc-hexane yielded a yellow solid.

(1b) \( R_f = 0.49 \) in 10% EtOAc-hexane; a yellow solid; Yield: 87%; m.pt.72°C; IR (KBr pellet): 2810, 1600, 1265, 1029, 804 cm⁻¹; \(^1\)HNMR (CDCl₃, 400MHz) δ: 7.71-7.60 (m, 2H, Ar), 7.29-7.20 (m, 4H, Ar), 6.69-6.62 (m, 2H, Ar), 4.20 (t, 2H, 1XOCH₂), 3.22 (t, 2H, 1XCH₂Br), 1.79-1.77 (m, 14H, 7XCH₂), 0.97 (t, 3H, 1XCH₃).

(1c) \( R_f = 0.51 \) in 10% EtOAc-hexane; a yellow solid; Yield: 81%; m.pt.64°C; IR (KBr pellet): 2800, 1600, 1255, 1025 and 804 cm⁻¹; \(^1\)H NMR (CDCl₃, 400MHz) δ: 7.71-7.62 (m, 2H, Ar), 7.29-7.20 (m, 4H, Ar), 6.69-6.62 (m, 2H, Ar), 4.21 (t, 2H, 1XOCH₂), 3.23 (t, 2H, 1XCH₂Br), 1.79-1.77 (m, 16H, 8XCH₂), 0.97 (t, 3H, 1XCH₃).

**General procedure for the synthesis of 4-(4-alkyloxybenzoyloxy)-1-benzyloxybenzene (2b)**

To a solution of 4-propyloxy benzoic acid (1 equiv, 0.001mol) and 4-benzyloxy phenol (1 equiv, 0.001 mol) in dichloromethane (50ml) under nitrogen atmosphere were added DCC (1 equiv, 0.001mol) and DMAP (0.00005 mol). The resulting reaction mixture was stirred at room temperature for 24 h. The urea formed during the reaction was removed by filtration and the dichloromethane was evaporated in vacuo. The crude product obtained was purified by column
chromatography using silica gel (100 – 200 mesh) as stationary phase and a mixture of 30% CH₂Cl₂-hexane as a mobile phase. The esters were further purified by repeated crystallization in a mixture of CH₂Cl₂-ethanol (9:1) to obtain pure compound.

4-(4-propyloxybenzoyloxy)-1-benzyloxybenzene

\[ R_f = 0.29 \text{ in 20\% EtOAc-hexane; a white solid; Yield: 58\%}; \text{ m.p.126\(^\circ\)C; IR (KBr pellet): 3011, 2989, 1455, 1409, 1781, 1259, 798 cm}^{-1}; \text{ }^1\text{HNMR (CDCl}_3\text{,400MHz)} \delta: 8.02 (d, J=8.8 \text{ Hz, 2H, Ar}), 7.30 (m, 5H, Ar), 7.01 (m, 4H, Ar), 6.83 (d, 2H, J=9.0 \text{ Hz, Ar}), 5.01 (s, 2H, 1XCH}_2\text{), 3.95 (t, 2H, 1XOCH}_2\text{), 1.75 (m, 2H, 1XCH}_2\text{), 0.90 (t, 3H, 1XCH}_3\text{).} \]

4-(4-butyloxybenzoyloxy)-1-benzyloxybenzene

\[ R_f = 0.28 \text{ in 20\% EtOAc-hexane; a white solid; Yield: 58\%}; \text{ m.p.127\(^\circ\)C; IR (KBr pellet): 3011, 2989, 1456, 1409, 1781, 1259, 798 cm}^{-1}; \text{ }^1\text{HNMR (CDCl}_3\text{,400MHz)} \delta: 8.02 (d, J=8.8 \text{ Hz, 2H, Ar}), 7.30 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.83 (d, 2H, J=9.0 \text{ Hz, Ar}), 5.01 (s, 2H, 1XCH}_2\text{), 3.95 (t, 2H, 1XOCH}_2\text{), 1.75 (m, 4H, 2XCH}_2\text{), 0.90 (t, 3H, 1XCH}_3\text{).} \]

4-(4-pentyloxybenzoyloxy)-1-benzyloxybenzene

\[ R_f = 0.29 \text{ in 20\% EtOAc-hexane; a white solid; Yield: 61\%}; \text{ m.p.120\(^\circ\)C; IR (KBr pellet): 3011, 2989, 1456, 1409, 1787, 1259, 798 cm}^{-1}; \text{ }^1\text{HNMR (CDCl}_3\text{,400MHz)} \delta: 8.02 (d, J=8.8 \text{ Hz, 2H, Ar}), 7.30 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 \text{ Hz, Ar}), 5.01 (s, 2H, 1XCH}_2\text{), 3.95 (t, 2H, 1XOCH}_2\text{), 1.75 (m, 6H, 3XCH}_2\text{), 0.90 (t, 3H, 1XCH}_3\text{).} \]
4-(4-hexyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.29$ in 20% EtOAc-hexane; a white solid; Yield: 63%; m.p.118°C; IR (KBr pellet): 3014, 2989, 1456, 1409, 1787, 1259, 799 cm$^{-1}$; $^1$HNMR (CDCl$_3$,400MHz) δ: 8.02 (d, J=8.8 Hz, 2H, Ar), 7.30 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.01 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.75 (m, 8H, 4XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).

4-(4-heptyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.28$ in 20% EtOAc-hexane; a white solid; Yield: 62%; m.p.117°C; IR (KBr pellet): 3014, 2989, 1456, 1419, 1787, 1259, 799 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.03 (d, J=8.8 Hz, 2H, Ar), 7.30 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.01 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.75 (m, 10H, 5XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).

4-(4-octyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.30$ in 20% EtOAc-hexane; a white solid; Yield: 65%; m.p.115°C; IR (KBr pellet): 3014, 2989, 1456, 1419, 1785, 1259, 799 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.03 (d, J=8.8 Hz, 2H, Ar), 7.30 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.02 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.75 (m, 12H, 6XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).

4-(4-nonyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.28$ in 20% EtOAc-hexane; a white solid; Yield: 66%; m.p.112°C IR (KBr pellet): 3014, 2989, 1456, 1419, 1785, 1259, 799 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.03 (d, J=8.8 Hz, 2H, Ar), 7.31 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.02 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.75 (m, 14H, 7XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).
4-(4-decyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.28$ in 20% EtOAc-hexane; a white solid; Yield: 69%; m.p.109°C; IR (KBr pellet): 3015, 2989, 1458, 1419, 1785, 1259, 799 cm$^{-1}$. $^1$HNMR (CDCl$_3$, 400MHz) $\delta$: 8.03 (d, J=8.8 Hz, 2H, Ar), 7.31 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.02 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.75 (m, 16H, 8XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).

4-(4-undecyloxybenzoyloxy)-1-benzyloxybenzene

$R_f = 0.29$ in 20% EtOAc-hexane; a white solid; Yield: 73%; m.p.104°C; IR (KBr pellet): 3015, 2989, 1458, 1419, 1785, 1259, 799 cm$^{-1}$. $^1$HNMR (CDCl$_3$, 400MHz) $\delta$: 8.03 (d, J=8.8 Hz, 2H, Ar), 7.31 (m, 5H, Ar), 7.02 (m, 4H, Ar), 6.84 (d, 2H, J=9.0 Hz, Ar), 5.02 (s, 2H, 1XCH$_2$), 3.95 (t, 2H, 1XOCH$_2$), 1.76 (m, 18H, 9XCH$_2$), 0.90 (t, 3H, 1XCH$_3$).

General procedure for the synthesis of 4-(4-alkyloxybenzoyloxy) phenol (2c)

4-(4-propyloxybenzoy-loxy)-1-benzyloxybenzene (1 equiv, 0.015 mol) was dissolved in freshly distilled ethyl acetate, and 10% Pd/C catalyst (0.05 g) was hydrogenated over a period of 14 hours. The reaction mixture was filtered on a celite bed and the filtrate was evaporated to dryness in vacuo to furnish the pure product.

4-(4-propyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 44%; m.p.129°C; IR (KBr pellet): 3150, 2926, 1501, 1400, 1968, 802 cm$^{-1}$. $^1$HNMR (CDCl$_3$, 400MHz) $\delta$: 8.10 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.82 (d, 2H, J=7.0Hz, Ar), 5.31 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.63 (t, 2H, 1XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).
4-(4-butyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 43%; m.p.126°C; IR (KBr pellet): 3152, 2926, 1501, 1400, 1968, 804 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ:

8.10 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.82 (d, 2H, J=7.0Hz, Ar), 5.31 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 4H, 2XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).

4-(4-pentyloxybenzoyloxy) phenol

$R_f = 0.30$ in 50% EtOAc-hexane; a white solid; Yield: 45%; m.p.123°C; IR (KBr pellet): 3152, 2926, 1503, 1400, 1968, 804 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ:

8.10 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.82 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 6H, 3XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).

4-(4-hexyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 46%; m.p.120°C; IR (KBr pellet): 3152, 2928, 1503, 1400, 1968, 804 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ:

8.11 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.82 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 8H, 4XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).

4-(4-heptyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 48%; m.p.119°C; IR (KBr pellet): 3152, 2928, 1503, 1400, 1968, 804 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ:

8.11 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.82 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.63 (t, 10H, 5XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).
4-(4-octyloxybenzoyloxy) phenol

$R_f = 0.29$ in 50% EtOAc-hexane; a white solid; Yield: 49%; m.p.117°C; IR (KBr pellet): 3152, 2928, 1503, 1405, 1968, 807 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.11 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.83 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 12H, 6XCH$_2$), 0.92 (t, 3H, 1XCH$_3$).

4-(4-nonyloxybenzoyloxy) phenol

$R_f = 0.30$ in 50% EtOAc-hexane; a white solid; Yield: 50%; m.p.113°C; IR (KBr pellet): 3150, 2928, 1503, 1405, 1965, 807 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.11 (d, 2H, J= 8.8Hz, Ar), 7.03 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.83 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 14H, 7XCH$_2$), 0.93 (t, 3H, 1XCH$_3$).

4-(4-decyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 53%; m.p.112°C; IR (KBr pellet): 3150, 2928, 1503, 1405, 1965, 807 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.11 (d, 2H, J= 8.8Hz, Ar), 7.02 (d, 2H, J=7.0 Hz, Ar), 6.93 (d, 2H, J=7.2Hz, Ar), 6.83 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 16H, 8XCH$_2$), 0.93 (t, 3H, 1XCH$_3$).

4-(4-undecyloxybenzoyloxy) phenol

$R_f = 0.31$ in 50% EtOAc-hexane; a white solid; Yield: 55%; m.p.110°C; IR (KBr pellet): 3150, 2928, 1503, 405, 1965, 809 cm$^{-1}$; $^1$HNMR (CDCl$_3$, 400MHz) δ: 8.11 (d, 2H, J= 8.8Hz, Ar), 7.02 (d, 2H, J=7.0 Hz, Ar), 6.94 (d, 2H, J=7.2Hz, Ar), 6.83 (d, 2H, J=7.0Hz, Ar), 5.32 (s, 1H, OH), 4.01 (t, 2H, 1XOCH$_2$), 1.62 (t, 18H, 9XCH$_2$), 0.93 (t, 3H, 1XCH$_3$).
General procedure for the synthesis of 4-[7-[4(4-Butyl-phenylazo)-phenoxy]-alkyloxy]-benzoic acid 4-decyloxy-phenylester (A-3 to A-11 and B-3 to B11)

A mixture of 4-ω-bromo alkyloxy-4-butylobenzene (1 equiv, 0.23 mol), 4-(4-undecyloxybenzoyloxy) phenol (1.2 equiv, 0.276 mol) and anhydrous K$_2$CO$_3$ (2 equiv, 0.92 mol), in 10ml of DMF was stirred at 85°C for 22 hours. The reaction mixture was cooled to room temperature and poured into ice cold water. The aqueous layer was extracted into CH$_2$Cl$_2$. The combined organic layer was then washed with brine and dried over anhydrous Na$_2$SO$_4$. Evaporation of solid gave an orange coloured solid, which was repeatedly recrystallized by a mixture of EtOH-CH$_2$Cl$_2$.

A-3

Yield: 55 %: a yellow solid [found C, 75.7; H, 7.51; N, 4.32. C$_{40}$H$_{48}$N$_2$O$_5$ requires C, 75.44; H, 7.60; N, 4.40]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679 cm$^{-1}$. $^1$H NMR (CDCl$_3$,400MHz) δ: 8.14 (d, J=9.2Hz, 2H, Ar), 7.90 (d, J=7.6Hz, 2H, Ar) ,7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8.8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.00 - 6.90 (m, 6H, Ar), 4.06 - 3.96 (m, 4H, 2XOCH$_2$), 2.69 (t, 2H, 1XOCH$_2$), 1.84 -1.40 (m, 18H, 9XCH$_2$), 0.96 - 0.94 (m, 6H, 2XCH$_3$); C$^{13}$NMR (100 MHz,CDCl$_3$): 171.5, 169.8, 161.5, 158.6, 133,0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

A-4

Yield: 61 %: a yellow solid [found C, 75.36; H, 7.65; N, 4.25. C$_{41}$H$_{50}$N$_2$O$_5$ requires C, 75.66; H, 7.74; N, 4.30]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679 cm$^{-1}$. $^1$H NMR (CDCl$_3$,400MHz) δ: 8.14 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J= 8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.00 - 6.90 (m, 6H, Ar), 4.06 - 3.96 (m, 4H, 2XOCH$_2$), 2.69 (t, 2H, 1XOCH$_2$), 1.84 -1.40 (m, 18H, 9XCH$_2$), 0.96 - 0.94 (m, 6H, 2XCH$_3$); C$^{13}$NMR (100 MHz,CDCl$_3$): 171.5, 169.8, 161.5, 158.6, 133,0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.
2H, Ar), 7.08 - 6.90 (m, 6H, Ar), 4.06 - 3.96 (m, 4H, 2XOCH$_2$), 2.67 (t, 2H, 1XOCH$_2$), 1.84 - 1.36 (m, 20H, 10XCH$_2$), 0.96 - 0.94 (m, 6H, 2XCH$_3$).

$^{13}$C NMR (100 MHz,CDCl$_3$): 171.5, 169.8, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

A-5

Yield: 63 %: a yellow solid [found C, 76.02; H, 7.81; N, 4.17.C$_{42}$H$_{52}$N$_2$O$_5$ requires C, 75.87; H, 7.88; N, 4.21]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679 cm$^{-1}$.$^1$H NMR (CDCl$_3$,400MHz) δ: 8.13(d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08 - 6.90 (m, 6H, Ar), 4.06 - 3.96 (m, 4H, 2XOCH$_2$), 2.67 (t, 2H, 1XOCH$_2$), 1.84 - 1.83 (m, 22H, 12XCH$_2$), 0.96 - 0.94 (m, 6H, 2XCH$_3$).$^{13}$NMR (100 MHz,CDCl$_3$): 171.5, 169.7, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

A-6

Yield: 65 %: a yellow solid [found C, 76.39; H, 8.02; N, 4.11.C$_{43}$H$_{54}$N$_2$O$_5$ requires C, 76.07; H, 8.02; N, 4.13]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 687 cm$^{-1}$.$^1$H NMR (CDCl$_3$,400MHz) δ:8.13 (d, J=7.6Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 6.98 - 6.90 (m, 6H, Ar), 4.03 (m, 4H, 1XOCH$_2$), 2.67 (t, 2H, 1XOCH$_2$), 1.84 - 1.40 (m, 24H, 12XCH$_2$), 0.96 - 0.94 (m, 6H, 2XCH$_3$).$^{13}$NMR (100 MHz,CDCl$_3$): 171.5, 169.8, 161.5, 158.5, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.
A-7

Yield: 70 %: a yellow solid [found C, 76.37; H, 7.69; N, 4.01.\text{C}_4\text{H}_6\text{N}_2\text{O}_5\text{ requires}
C, 76.27; H, 8.15; N, 4.04]; IR (KBr pellet): 2937, 1729, 1249, 1081, 841, 687
\text{cm}^{-1}.\text{H NMR (CDCl}_3,400\text{MHz}) \delta:  8.15 \text{ (d, J=9.2Hz, 2H, Ar), 7.90 \text{ (d, J=8.8Hz, 2H, Ar), 7.80 \text{ (d, J=8.4Hz, 2H, Ar), 7.30 \text{ (d, J=8Hz, 2H, Ar), 7.10 \text{ (d, J=6.8Hz, 2H, Ar), 6.98 – 6.90 \text{ (m, 6H, Ar), 4.06 – 4.01 \text{ (m, 4H, 2XOCH}_2\text{), 2.67 \text{ (t, 2H, 1XOCH}_2\text{), 1.84 - 1.40 \text{ (m, 26H, 13XCH}_2\text{), 0.97-0.94 \text{ (m, 6H, 2XCH}_3\text{)}. C}^{13}\text{NMR (100 MHz,CDCl}_3\text{): 171.5, 169.8, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.}]

A-8

Yield: 76 %: a yellow solid [found C, 76.67; H, 7.81; N, 43.89.\text{C}_4\text{H}_6\text{N}_2\text{O}_5\text{ requires}
C, 76.45; H, 8.27; N, 3.96]; IR (KBr pellet): 2937, 1729, 1249, 1080, 841, 687 \text{cm}^{-1}.\text{H NMR (CDCl}_3,400\text{MHz}) \delta:  8.13 \text{ (d, J=8.4Hz, 2H, Ar), 7.90 \text{ (d, J=8.8Hz, 2H, Ar), 7.80 \text{ (d, J=8.4Hz, 2H, Ar), 7.30 \text{ (d, J=8Hz, 2H, Ar), 7.10 \text{ (d, J=6.8Hz, 2H, Ar), 6.98 – 6.90 \text{ (m, 6H, Ar), 4.06 – 4.01 \text{ (m, 4H, 2XOCH}_2\text{), 2.69 – 2.65 \text{ (t, 2H, 1XOCH}_2\text{), 1.8 - 1.3 \text{ (m, 28H, 14XCH}_2\text{), 0.96 - 0.94 \text{ (m, 6H, 2XCH}_3\text{)}. C}^{13}\text{NMR (100 MHz,CDCl}_3\text{): 171.5, 169.8, 163.5, 158.6, 132.0, 129.2, 122.6, 117.7, 75.3, 56.7, 50.0, 37.1, 32.6, 31.3, 26.8, 22.5 and 20.0.}]

A-9

Yield: 71%: a yellow solid [found: C, 76.93; H, 8.01; N; 3.81.\text{C}_4\text{H}_6\text{N}_2\text{O}_5\text{ requires}
C, 76.63; H, 8.39; N, 3.89 ]; IR (KBr pellet): 2934, 1735, 1249, 1080, 841, 687 \text{cm}^{-1}.\text{H NMR (CDCl}_3,400\text{MHz}) \delta:  8.13 \text{ (d, J=8.4Hz, 2H, Ar), 7.90 \text{ (d, J=8.8Hz, 2H, Ar), 7.80 \text{ (d, J=8.4Hz, 2H, Ar), 7.30 \text{ (d, J=8Hz, 2H, Ar), 7.10 \text{ (d, J=6.8Hz, 2H, Ar), 6.98 – 6.90 \text{ (m, 6H, Ar), 4.06 – 4.01 \text{ (m, 4H, 1XOCH}_2\text{), 2.69 –}
2.65 (t, 2H, 1XOCH₂), 1.84 - 1.40 (m, 30H, 15XCH₂), 0.97 - 0.93 (m, 6H, 2XCH₃). C¹³NMR (100 MHz, CDCl₃): 171.5, 169.8, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

A-10

Yield: 72%; a yellow solid [found: C, 77.05; H, 8.38; N, 3.76.C₄₇H₆₂N₂O₅ requires C, 76.80; H, 8.50; N, 3.81]; IR (KBr pellet): 2934, 1738, 1248, 1080, 840, 690 cm⁻¹. ¹H NMR (CDCl₃, 400MHz) δ: 8.13 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08 – 6.90 (m, 6H, Ar), 4.06 – 4.01 (m, 4H, 2XOCH₂), 2.69 (t, 2H, 1XOCH₂), 1.84 -1.40 (m, 32H, 16XCH₂), 0.95 -0.92 (m, 6H, 2XCH₃). C¹³NMR (100 MHz, CDCl₃): 171.5, 169.8, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

A-11

Yield: 72%; a yellow solid [found: C, 77.21; H, 8.31; N, 3.65.C₄₈H₆₄N₂O₅ requires C, 76.97; H, 8.61; N, 3.74]; IR (KBr pellet): 2944, 1738, 1248, 1078, 840, 690 ¹H NMR (CDCl₃, 400MHz) δ: 8.13 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08 – 6.90 (m, 6H, Ar), 4.03 (m, 4H, 2XOCH₂), 2.69 – 2.65 (t, 2H, 1XOCH₂), 1.84 - 1.40 (m, 34H, 17XCH₂), 0.95 -0.92 (m, 6H, 2XCH₃). C¹³NMR (100 MHz, CDCl₃): 171.5, 169.8, 161.5, 158.6, 133.0, 129.2, 122.6, 117.7, 75.3, 56.7, 49.0, 37.1, 32.6, 31.3, 26.8, 21.8, 20.0 and 14.2.

B-3

Yield: 51%; a yellow solid [found C, 75.42; H, 7.22; N, 4.41.C₃ₙH₄₆N₂O₅ requires C, 75.21; H, 7.44; N, 4.50]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679
\( ^1H\) NMR (CDCl\(_3\), 400MHz) \( \delta \): 8.11 (d, J=8.8Hz, 2H, Ar), 7.88 (d, J=8.8Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.00-6.90 (m, 6H, Ar), 4.06-3.96 (m, 4H, 2XOCH\(_2\)), 2.69-2.65 (t, 2H, 1XOCH\(_2\)), 1.84-1.36 (m, 20H, 10XCH\(_2\)), 0.96 -0.94 (m, 6H, 2X CH\(_3\)).

\( ^{13}C\) NMR (100 MHz,CDCl\(_3\)): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-4**

Yield: 55 %: a yellow solid [found C, 75.7; H, 7.51; N, 4.32].\( ^{13}C\)\(_{40}\)H\(_{48}\)N\(_2\)O\(_5\) requires C, 75.44; H, 7.60; N, 4.40]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679 cm\(^{-1}\).\( ^1H\) NMR (CDCl\(_3\),400MHz) \( \delta \): 8.14 (d, J=9.2Hz, 2H, Ar), 7.90 (d, J=7.6Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8.8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08 - 6.90 (m, 6H, Ar), 4.06-3.96 (m, 4H, 1XOCH\(_2\)), 2.69-2.65 (t, 2H, 1XOCH\(_2\)), 1.84-1.40 (m, 22H, 11XCH\(_2\)), 0.96 -0.94 (m, 6H, 2 X CH\(_3\)). \( ^{13}C\) NMR (100 MHz ,CDCl\(_3\)): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-5**

Yield: 63 %: a yellow solid [found C, 75.36; H, 7.67; N, 4.25].\( ^{13}C\)\(_{41}\)H\(_{50}\)N\(_2\)O\(_5\) requires C, 75.66; H, 7.74; N, 4.30]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 679 cm\(^{-1}\).\( ^1H\) NMR (CDCl\(_3\),400MHz) \( \delta \): 8.13 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.87 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08-6.90 (m, 6H, Ar), 4.06-3.96 (m, 4H, 2XOCH\(_2\)), 2.69-2.65 (t, 2H, 1XOCH\(_2\)), 1.84-1.36 (m, 24H, 12 X CH\(_2\)), 0.96 -0.94 (m, 6H, 2X CH\(_3\)).

\( ^{13}C\) NMR (100 MHz,CDCl\(_3\)): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2
**B-6**

Yield: 76 %: a yellow solid [found C, 76.02; H, 7.81; N, 4.16.C_{42}H_{52}N_{2}O_{5} requires C, 75.87; H, 7.88; N, 4.21]; IR (KBr pellet): 2937, 1729, 1249, 1080, 841, 687 cm⁻¹.¹H NMR (CDCl₃,400MHz) δ : 8.13 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J= 8Hz, 2H, Ar), 7.10 (d, J = 6.8Hz, 2H, Ar), 6.98-6.90 (m, 6H, Ar), 4.06-4.01 (m, 4H, 1XOCH₂), 2.69-2.65 (t, 2H, 1XOCH₂), 1.84-1.36 (m, 26H, 13XCH₂), 0.96 - 0.94 (m, 6H, 2XCH₃).C¹³NMR (100 MHz, CDCl₃): 169.7, 163.9, 159.6, 141.0,133.0, 129.2 124.6,122.6, 115.7,111.0, 75.367.6, 55.137.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-7**

Yield: 65 %: a yellow solid [found C, 76.39; H, 8.03; N, 4.11.C_{43}H_{54}N_{2}O_{5} requires C, 76.07; H, 8.02; N, 4.13]; IR (KBr pellet): 2941, 1734, 1249, 1084, 841, 687 cm⁻¹.¹H NMR (CDCl₃,400MHz) δ: 8.15 (d, J=7.6Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar ),7.87 (d, J=8.4 Hz, 2H, Ar), 7.28 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 6.98-6.90 (m, 6H, Ar), 4.06-4.01 (m, 4H, 1XOCH₂), 2.69-2.65 (t, 2H,1XOCH₂), 1.84-1.40 (m, 28H, 14XCH₂), 0.96-0.94 (m, 6H, 2XCH₃).C¹³NMR (100 MHz, CDCl₃): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.

**B-8**

Yield: 71 %: a yellow solid [found C, 76.37; H, 7.69; N, 4.01.C_{44}H_{56}N_{2}O_{5} requires C, 76.27; H, 8.15; N, 4.04]; IR (KBr pellet): 2937, 1729, 1249, 1081, 841, 687 cm⁻¹.¹H NMR (CDCl₃,400MHz) δ: 8.13 (d, J=9.2Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.87 (d, J= 8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 6.98 - 6.90 (m, 6H, Ar), 4.06-4.01 (m, 4H, 2XOCH₂), 2.69-2.65 (t,
2H,1XOCH\textsubscript{2}), 1.84-1.40 (m, 30H, 15XCH\textsubscript{2}), 0.97 -0.94 (m, 6H, 2XCH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz,CDCl\textsubscript{3}): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-9**

Yield: 71%; a yellow solid [found: C, 76.67; H, 8.07; N; 3.89.C\textsubscript{45}H\textsubscript{88}N\textsubscript{2}O\textsubscript{5} requires C,76.45; H, 8.27; N, 3.96]; IR (KBr pellet): 2934, 1735, 1249, 1080, 841, 687 cm\textsuperscript{-1}.\textsuperscript{1}H NMR (CDCl\textsubscript{3},400MHz) δ: 8.13 (d, J=8.4Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar),7.80 (d, J=8.4Hz, 2H, Ar), 7.30 (d, J=8 Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 6.94 (m, 6H, Ar), 4.06-4.01 (m, 4H, 2XOCH\textsubscript{2}), 2.67 (t, 2H, 1XOCH\textsubscript{2}), 1.84-1.40 (m, 32H, 16XCH\textsubscript{2}), 0.97 -0.93 (m, 6H, 2X CH\textsubscript{3}). \textsuperscript{13}C NMR (100MHz, CDCl\textsubscript{3}): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-10**

Yield: 76%; a yellow solid [found: C, 76.83; H, 8.01; N; 3.81.C\textsubscript{46}H\textsubscript{60}N\textsubscript{2}O\textsubscript{5} requires C, 76.63; H, 8.39; N, 3.89]; IR (KBr pellet): 2934, 1738, 1248, 1080, 840, 690 cm\textsuperscript{-1}.\textsuperscript{1}H NMR (CDCl\textsubscript{3},400MHz) δ: 8.13 (d, J=8.8Hz, 2H, Ar), 7.90 (d, J=8.8Hz, 2H, Ar), 7.87 (d, J= 8.4Hz, 2H, Ar), 7.30 (d, J=8Hz, 2H, Ar), 7.10 (d, J=6.8Hz, 2H, Ar), 7.08 (m, 6H, Ar), 4.03 (m, 4H, 2XOCH\textsubscript{2}), 2.65 (t, 2H, 2XOCH\textsubscript{2}), 1.84 - 1.40 (m, 34H, 17XCH\textsubscript{2}), 0.96 - 0.92 (m, 6H, 2XCH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz,CDCl\textsubscript{3}): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2

**B-11**

Yield: 72%; a yellow solid [found: C, 77.35; H, 8.38; N, 3.75 .C\textsubscript{47}H\textsubscript{62}N\textsubscript{2}O\textsubscript{5} requires C, 76.80; H, 8.50; N, 3.81]; IR (KBr pellet): 2944, 1738, 1248, 1078,
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 8.11 (d, J=8.8 Hz, 2H, Ar), 7.90 (d, J=8.8 Hz, 2H, Ar), 7.80 (d, J=8.4 Hz, 2H, Ar), 7.30 (d, J = 8 Hz, 2H, Ar), 7.10 (d, J=6.8 Hz, 2H, Ar), 7.08 (m, 6H, Ar), 4.0 (m, 4H, 2XOCH$_2$), 2.6 (t, 2H, 2XOCH$_2$), 1.8 - 1.4 (m, 36H, 18XCH), 0.95 - 0.92 (m, 6H, 2XCH$_3$). $^{13}$NMR (100 MHz, CDCl$_3$): 169.7, 163.9, 159.6, 141.0, 133.0, 129.2, 124.6, 122.6, 115.7, 111.0, 75.3, 67.6, 55.1, 37.1, 32.6, 30.6, 26.5, 22.5 and 14.2
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