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PII: S0040-4020(16)30409-4

DOI: 10.1016/j.tet.2016.05.024

Reference: TET 27751

To appear in: *Tetrahedron*

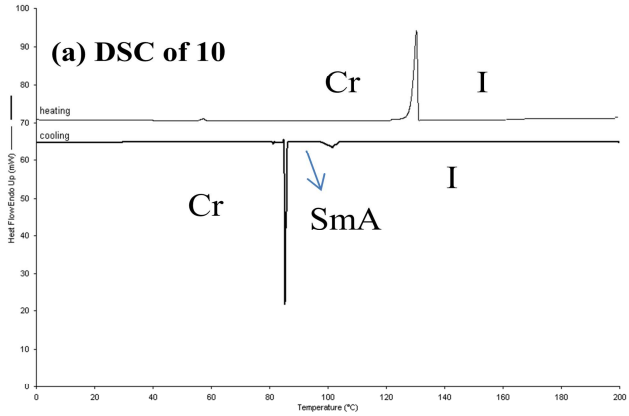
Received Date: 2 January 2016

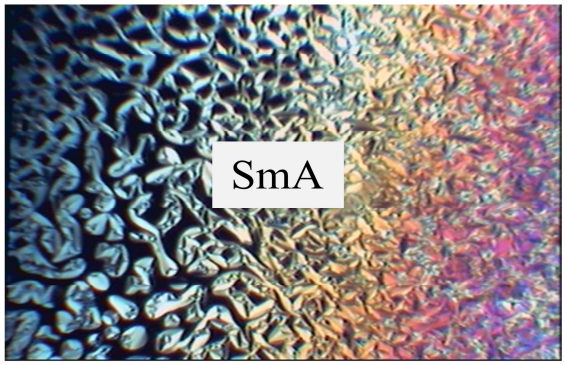
Revised Date: 29 April 2016

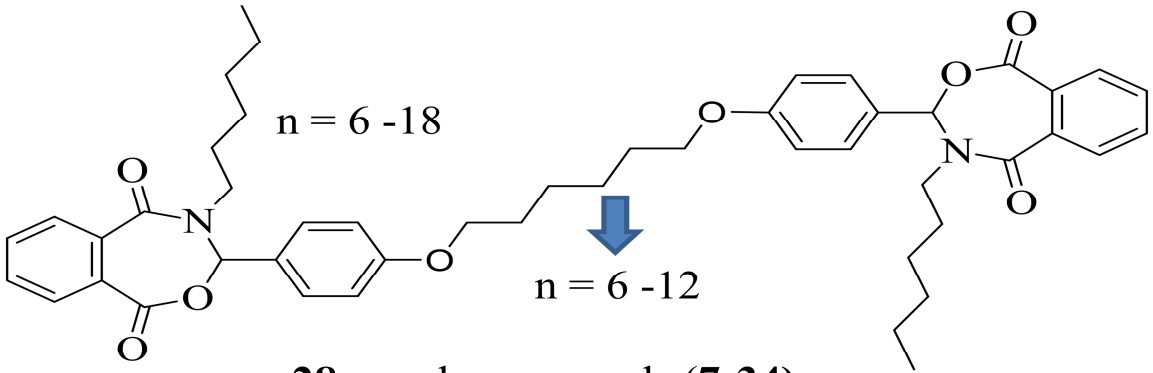
Accepted Date: 9 May 2016

Please cite this article as: Mohammad A-T, Srinivasa HT, Hariprasad S, Yeap G-Y, Enhanced liquid crystal properties in symmetric ethers containing the oxazepine core: synthesis and characterization of seven member heterocyclic dimers, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.05.024.

Graphical abstract







28 novel compounds (**7-34**)

Enhanced liquid crystal properties in symmetric ethers containing the oxazepine core: Synthesis and characterization of seven member heterocyclic dimers

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Abstract

Four new series of symmetric dimers derived from the basic heterocyclic oxazepine core were designed, synthesized, characterized and investigated for liquid crystal properties. The chemical structures of the prepared molecules were characterized by infrared, $^{1}H/^{13}C$ nuclear magnetic resonance spectra and elemental analysis. Thermal properties and mesophase textures were evaluated by using a combination of differential scanning calorimetry and polarized optical microscopy techniques. Most of the compounds exhibited monotropic liquid crystalline phases in cooling processes. The effect of the spacer chain length and terminal alkoxy chain were studied for the influence on the type of mesophase formed by the homologous series of compounds. Lower members possessing the methylene spacer and a terminal alkoxy- chain favoured smectogenic properties; those derived from medium methylene spacer with terminal alkoxy chain favoured nematogenic properties whereas molecules derived with a higher methylene spacer with terminal alkoxy chain members did not favour any liquid crystalline properties.

Keywords: mesophase; oxazepine; heterocycle; dimers; smectic; methylene spacers.

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1. Introduction

The simplest form of oligomer liquid crystal is dimeric, in which the main part of the molecule contains two rigid mesogenic/non-mesogenic units connected via a flexible spacer.[1,2] Several classes of dimeric liquid crystals have been prepared, studied extensively and documented.[3-7] They have attracted enormous attention during the past decade due to their interesting liquid crystalline properties.[8-10] A dramatic increase in the diversity of molecular architectures comprise rod-, disk- and banana-shaped derived dimeric and oligomeric mesogenic units. These units are known to exhibit LC behaviour with supramolecular structures.[11-17] Imrie's review illustrates that the structure-property relationship of various dimers/oligomers and the dimers themselves have attracted attention as they display an unusual interesting mesomorphism different to that of the corresponding monomers.[18] Furthermore, they have the ability to act as model compounds for semi-flexible, main-chain/side-chain liquid crystalline oligomers and polymers.[19] The majority of the symmetrical dimers possess mesogenic/non-mesogenic units which assure the mesophase with flexible spacer.

The effects of different spacers on the mesomorphic properties of symmetrical and unsymmetrical liquid crystalline dimers containing alkoxy-, cyanobiphenyl- and naphthalene systems are reported.[21,22] In connection to dimers, an ether linkage between the mesogenic/non-mesogenic unit and the central methylene spacer usually produces nematic behaviour, whereas an ester linkage induces smectic properties in the system.[20] It is generally observed that nematic-isotropic transition temperatures are higher for compounds with an alkoxy chain than for alkyl chain derivatives with the same total number of carbon atoms. This difference is attributed to the higher anisotropy of the molecular polarizability expected for an ether linkage in comparison with a methylene group.[23]

In this regard, there are few reports which deal with heterocyclic cores held by methylene spacers.[24] To date, a large number of symmetrical and non-symmetrical dimers have been reported with conventional aromatic cores, but there exists a scarcity of heterocyclic ring derived dimeric liquid crystals.[26-29] There exists one report of molecules that mimic the Archaea domain which were constructed by tetraether glycolipid analogues. This study inspired us to

explore the preparation of rigid blunt end derived oxazepine heterocyclic compounds for LC studies. The idea is a very similar approach to that shown by Plusquellec et al.[25]

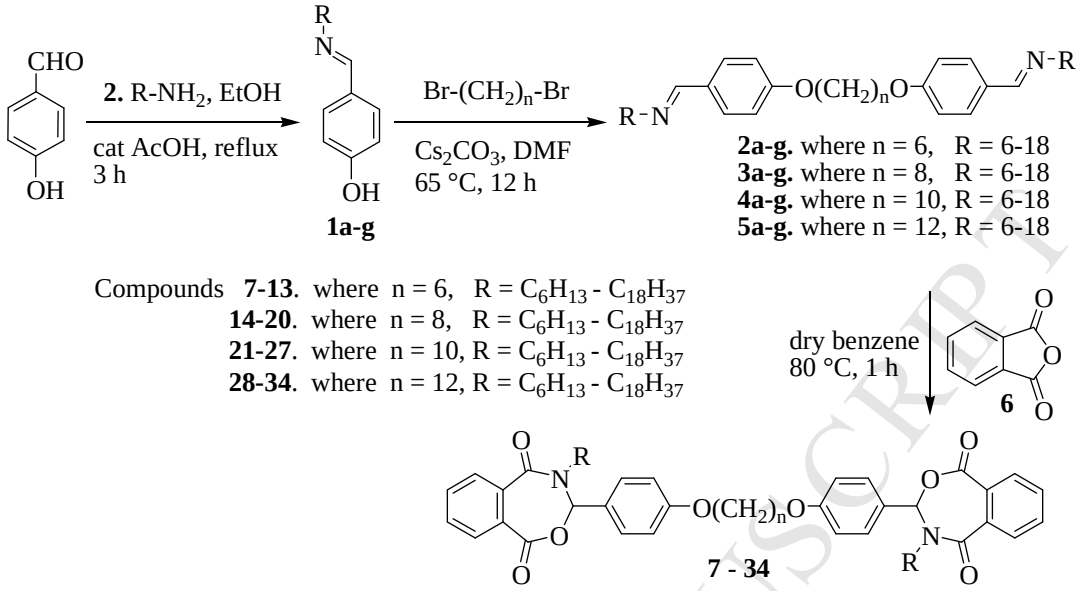
From a heterocyclic chemistry point of view and for their applicability as liquid crystals, we have studied the oxazepine heterocyclic ring and evaluated it for LC property with exhaustive chemical structure modifications.[30-33] The oxazepine heterocycle by itself hardly exhibits any LC property in many of its derivatives due to its unconventional size of being a seven membered polar heterocyclic ring. However, due to the easy synthesis of the oxazepine heterocycle, we were interested to extend the work to achieve interesting liquid crystals. The liquid crystals would then possess two oxazepine heterocycles which are connected and terminated by flexible alkylene spacers to attain low transition temperatures.

In this article, we present a strategy which reports the synthesis and mesomorphic properties of a new series of heterocyclic oxazepine dione ring derived symmetrical dimeric molecules in which a flexible spacer ranges from n = 6 - 12 carbon atoms and a terminal alkoxy chain ranges from n = 6 - 18 carbon atoms.

2. Results and discussion

2.1 Synthesis

The preparative pathway towards obtaining title compounds **7-34** is shown in Scheme 1. Imines **1a-g** were synthesised via a condensation reaction in a similar manner as reported earlier.[34] Compounds **2a-g, 3a-g, 4a-g** and **5a-g** resulted from Williamson's etherification between imines **1a-g** and various α,ω-dibromoalkanes ranging from $C_6H_{12}Br_2$ to $C_{12}H_{24}Br_2$.[30-34] The freshly prepared compounds **2a-g, 3a-g, 4a-g** and **5a-g** were subsequently reacted with phthalic anhydride to yield the target compounds **7-34**.



Scheme 1. Synthetic pathway for symmetric ethers containing the oxazepine core **7-34**.

Table 1. Thermotropic behaviours of symmetric oxazepine derivatives **7-34**.

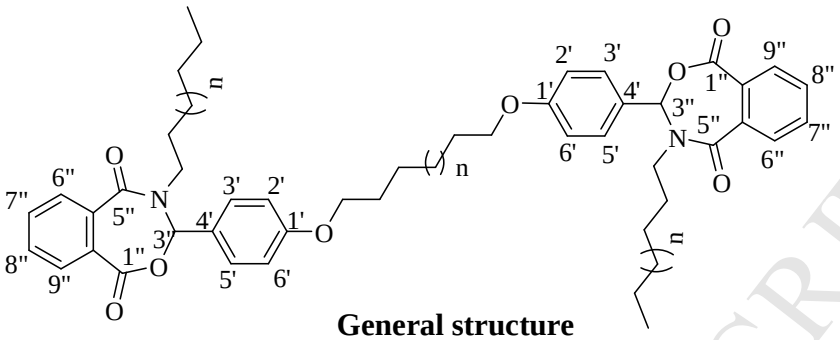
No	n/R	Heating scan and Cooling scan (onset 5 °C /min, [°C] / ΔH [kJ/mol])	
7	6/6	Cr 126.1 (70.10) I	Cr 94.3 (-55.23) I
8	6/8	Cr 130.4 (76.13) I	Cr 98.7 (-44.20) SmA 112.3 (-6.22) I
9	6/10	Cr 134.8 (59.20) I	Cr 87 (-83.45) SmA 103.9 (-8.23) I
10	6/12	Cr 137.1 (62.14) I	Cr 84.2 (-70.90) SmA 113.3 (-5.67) I
11	6/14	Cr 145.2 (42.67) I	Cr 89.3 (-42.67) N 117.3 (-7.11) I
12	6/16	Cr_1 95.2 (20.32) Cr_2 151.8 (88.43) I	Cr_1 93.6 (-34.41) N 123.6 (-6.20) I
13	6/18	Cr_1 93.2 (14.60) Cr_2 161.4 (48.09) I	Cr_1 78.1 (-20.22) Cr_2 120 (-52.20) I
14	8/6	Cr_1 132.5 (25.60) I	Cr 89.2 (-44.11) I
15	8/8	Cr 137.6 (48.90) I	Cr 94.3 (-33.43) SmA 118.5 (-5.76) I
16	8/10	Cr_1 82.1 (21.45) Cr_2 143.78 (19.00) I	Cr_1 96.9 (-24.62) SmA 121.6 (-7.20) I
17	8/12	Cr_1 89.4 (37.61) Cr_2 147.39 (52.37) I	Cr 87.7 (-29.90) N 118.1 (-5.76) I
18	8/14	Cr_1 91.3 (25.51) Cr_2 153.40 (72.29) I	Cr 84.6 (-23.40) N 111.9 (-7.30) I
19	8/16	Cr_1 94.8 (27.18) Cr_2 162.71 (50.35) I	Cr_1 72.8 (-29.14) Cr_2 123.2 (-42.15) I
20	8/18	Cr_1 108.9 (50.31) Cr_2 167.64 (78.28) I	Cr_1 86.2 (-25.46) Cr_2 135.1 (-31.83) I
21	10/6	Cr 131.4 (48.31) I	Cr_1 86.4 (-28.10) SmA 108.5 (-6.30) I
22	10/8	Cr_1 136.5 (60.27) I	Cr_1 91.8 (-37.41) SmA 116.6 (-3.69) I

23	10/10	Cr_1 92.7 (23.49) Cr_2 140.6 (32.11) I	Cr 88.6 (-22.60) SmA 109.8 (-3.49) I
24	10/12	Cr_1 89.7 (22.10) Cr_2 149.4 (21.79) I	Cr_1 85.4 (-19.78) SmA 113.7 (-0.86) I
25	10/14	Cr_1 98.2 (34.67) Cr_2 156.5 (60.19) I	Cr_1 94.3 (-14.10) N 118.5 (-4.30) I
26	10/16	Cr_1 116.3 (18.94)Cr_2 163.7 (24.18) I	Cr_1 82.8 (-45.31) Cr_2 121.7 (-29.28) N 138.6 (-4.50) I
27	10/18	Cr_1 119.3 (48.29) Cr_2 171.6 (66.14) I	Cr_1 93.6 (-39.76) Cr_2 128.6 (-48.25) N 152.6 (-2.89) I
28	12/6	Cr_1 81.2 (26.50) Cr_2 142.5 (19.30) I	Cr 87.6 (-26.75) SmA 103.2 (-4.55) I
29	12/8	Cr_1 84.6 (28.10) Cr_2 147.4 (33.20) I	$Cr_1$73.2 (-52.18) Cr_2 93.9 (-15.64) SmA 116.5 (-3.78) I
30	12/10	Cr_1 96.4 (15.45) Cr_2 150.5 (17.39) I	Cr_1 82.3 (-67.20) Cr_2 103.7 (-18.07) N 128 (-4.79) I
31	12/12	Cr_1 112.8 (19.44) Cr_2 154.8 (19.78) I	Cr_1 73.5 (-79.20) Cr_2 98.7 (-48.85) N 129.4 (-2.82) I
32	12/14	Cr_1 118.4 (14.66) Cr_2 163.3 (29.41) I	Cr $_1$ 77.3 (-46.30) Cr_2 107.4 (-14.55) N 130.2 (-3.74) I
33	12/16	Cr_1 123.8 (28.76) Cr_2 168.6 (31.05) I	Cr_1 83.4 (-39.76) Cr_2 114.3 (-18.90) N 135.6 (-1.22) I
34	12/18	Cr_1 128.2 (15.20) Cr_2 174.8 (17.52) I	Cr_1 96.3 (-24.89) Cr_2 138.8 (-19.33) I

Note: Cr_1/Cr_2 = crystal to crystal transitions; SmA = smectic A phase; N = nematic phase; I = isotropic phase

2. 2 Characterization by FT-IR spectroscopy

The diagnostic absorption bands at 2944 and 2870 cm^{-1} in the FT-IR spectrum of **7** are assigned to the C-H asymmetric and symmetric stretching of the respective methylene spacers. At lower frequency, the carbonyl group (C=O) was observed at the frequency 1660 cm^{-1}. The presence of the aromatic rings was inferred from the absorption bands at 3007, 1600 and 1588 cm^{-1}. The strongest band is observed in the fingerprint region of 1266 cm^{-1} which can be attributed to the presence of two ether (O-CH_2) groups for every dimeric structure. The FTIR spectra of compounds **7-34** exhibit similar diagnostic bands as those observed in compound **7**. These values conform with those reported in the FT-IR spectra for various 1,3-oxazepine compounds reported elsewhere.[30-34]



General structure

2. 3 Characterization by NMR spectroscopy

The complete ^{1}H and ^{13}C NMR assignment of representative compounds **7-34** were obtained and substantiated by means of ^{1}H-^{1}H correlation spectroscopy (COSY), ^{1}H-^{13}C hetero nuclear multiple quantum correlation (HMQC), and ^{1}H-^{13}C hetero nuclear multiple bond correlation (HMBC) spectroscopic measurements, as described in the literature.[30-34]

The values of the ^{1}H NMR chemical shift for compounds **7-34** in DMSO solution are listed in the experimental section. A complete assignment for the title compounds can be described based on the representative compounds as shown in Scheme 1. A complete ^{1}H NMR assignment of compound **7** is described as an example. The presence of a singlet at δ = 9.80 ppm is attributable to the H3′ and 3″ proton in the heterocyclic ring. This can be further substantiated by the direct bond hetero nuclear correlation with C3′ and C3″ within the frequency δ = 90.72 ppm. The aromatic protons H2′ or H6′ can be observed as a doublet at δ = 7.10 ppm. The signals which appear as a doublet due to H3′ or H5′ are observed at δ = 7.31 ppm and the aromatic protons (H2′, H3′, H5′ and H6′) are equivalent. The aromatic protons H6″, H7″, H8″ and H9″ are found to be non-equivalent. The two doublets in the down-field region at (δ = 8.36 and δ = 7.56 ppm) are assigned to aromatic protons H6″ and H9″. The ^{1}H NMR spectrum of compound **7** shows two triplets at (δ = 7.81 and δ = 7.95 ppm) due to aromatic protons H7″ and H8″ respectively. This fact suggests that the molecule is symmetric. The triplet attributed to the methoxy protons of the spacer is evident at slightly higher field (δ = 4.08 ppm), while the two triplets at δ = 3.80 ppm and δ = 0.95 can be assigned to the methylene proton N-CH_2 and CH_3 in

both terminal alkyl chains. The subsequent methylene protons of the fragment and those of the spacer give rise to overlapping multiplets at δ = 1.31-1.94 ppm.

After assigning the protons of title compound **7-34**, ^{13}C-NMR spectroscopy was carried out along with DEPT 135. The ^{13}C NMR spectrum of compounds **7** indicate that the aromatic carbons give rise to different peaks within the frequency range of δ = 115.43-134.31 ppm. The aromatic quaternary carbon and its neighboring proton are assigned with the employment of HMBC experiment. The assignment of C1′ at δ = 159.21 ppm is based on its correlation with H3′ and H5′. The HMBC spectrum also show cross peaks of 1″ of the carbonyl group (C=O) with H7″ atoms at δ = 168.72 ppm and C5′ of the carbonyl group (C=O) with H8″. Peaks at δ = 90.73 ppm can be assigned to C3′ or C3″ in the heterocyclic ring. Diagnostic peaks observed at δ = 39.44 ppm indicate the presence of the methylene in (N-CH_2) from the alkyl linkage. Signals attributable to the methylene carbons of the spacer alkyloxy chain and terminal alkyl chains are observed within the range of δ = 22.14 ppm. Peaks due to the methyl carbons are observed δ = 15.23 ppm.

The results inferred from the IR and NMR spectral data of compounds **7-34** are found to be in agreement with the proposed structure as shown in Scheme 1.

2. 4 Thermal and optical studies

The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (Elmer Pyris 1 DSC) operating at a scanning rate of ± 5 °C min^{-1} on heating and cooling cycles respectively. Texture observation was carried out using Carl Zeiss Axioskop 40 optical microscope equipped with Linkam LTS350 hot stage and TMS94 temperature controller.

Mesomorphic properties of all the compounds **7-34** were determined by differential scanning calorimetry (DSC) measurements and polarised optical microscopy (POM). DSC curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of the measurements was satisfactory. The phase transition temperatures reported in this paper were the peak values of the transition on DSC curves. Phase identification was made by comparing the observed textures with those reported in the literature. The phase transition temperatures, the associated enthalpy changes and mesophase textures of **7-34** are

summarized in Table 1. Clear-cut transition temperatures for LC and non-LC molecules and textures could be obtained from DSC curves and POM observations for all of the compounds. They were in good agreement with each other for the heating/cooling cycles along with their enthalpies.

Compounds **7-13** have methylene spacer length n = 6 and terminal alkyl chain varying from n = 6-18. Compound **7** hardly exhibited any LC property, whereas compounds **8-10** showed SmA mesomorphism. The compound **8** upon heating transformed from a crystalline state to the isotropic state at 130.4 °C (ΔH = 76.13). When cooled from the isotropic state, the compound exhibited focal conics with striped texture with transition bars for the SmC phase. Since the focal conic stripes did not originate from the isotropic liquid, and were observed after cooling for some time from the isotropic state, the existence of the SmE phase is ruled out. This is depicted in Figure 2 (a) at 112.3 °C (ΔH = - 6.22), before finally re-crystallising at 98.7 °C (ΔH = - 44.20). Similar transitions were found for the compounds **9** and **10**. The DSC trace of **10** is shown in Figure 1 (a). Notable changes occured in the next members **11** and **12**. Compound **11** melts at 145.2 °C (ΔH = 42.67) which went to isotropic state, then it was cooled from the isotropic state at 117.3 °C (ΔH = -7.11). It shows mosaic texture for the nematic phase. Optical photomicrograph of compound **12** upon cooling displaying SmA at 106 °C is depicted in Figure 2 (b). Interestingly, the compound **13** did not show any LC property.

In the second set of compounds **14-20**, having methylene spacer length: n = 8 and terminal alkyl chain varying from n = 6-18, compound **14** hardly exhibited any LC property, whereas compounds **15-16** showed SmA mesomorphism. For example, the compound **15** melts directly to the isotropic state at 137.6 °C (ΔH = 48.90) without showing any mesophase. When it was cooled down from the isotropic state, the SmA phase appeared at 118.5 °C (ΔH = -5.76) and then crystallised at 94.3 °C (ΔH = -33.43) respectively. An optical photomicrograph of compound **15** displaying SmA phase upon cooling at 109 °C is shown in Figure 2(c) with the observation under POM. Compounds **17** and **18** shows nematic LC property with mosaic texture monotropically. The representative DSC thermogram of compound **18** as shown in Figure 1(b) in which two endothermic peaks at 91.3 °C (ΔH = 25.51) and 153.4 °C (ΔH = 72.29) and two exothermic peaks at 84.6 °C (ΔH = -23.40) and 111.9 °C (ΔH = -7.30) occurred corresponding to

Cr_1-Cr_2-I and I-N-Cr_2 transitions. Interestingly, in this set, two compounds **19** and **20** did not show any LC property.

In the third set of compounds **21-27** having methylene spacer length: n = 10 and terminal alkyl chain varying from n = 6-18, all the compounds favored monotropic LC property. Compound **21** and **22** has one crystal-crystal transition on heating scan, while in the cooling scan the SmA phase appeared at 108.5 °C (ΔH = -6.30) and 116.6 °C (ΔH = -3.69), and then crystallized at 86.4 °C (ΔH = -28.10) and 91.8 °C (ΔH = -37.41) respectively. In the case of **23-27**, two crystal-crystal transitions appeared on heating cycle as tabulated in Table 1. In this set, four compounds **21-24** favoured SmA mesomorphism from isotropic states. The DSC thermogram of compound **25** during heating run shows two peaks which can be ascribed as Cr_1-Cr_2-I at 98.2 °C (ΔH = 34.67) and 156.5 °C (ΔH = 60.19) and in the cooling scan, two peaks appeared at 94.3 °C (ΔH = -14.10) and 118.5 °C (ΔH = -4.30) for I-N-Cr_2 transitions respectively. Compound **26** and **27** show the nematic phase with two crystal-crystal transitions in the cooling scan.

From these observations, it is clear that the length of the alkoxy chain influences not only the nature of the mesophase, but also the mesomorphic temperature range. Generally, an increase in terminal length often results in an enhanced induced-dipole-induced-dipole interaction between the terminal chains, leading to the formation of a more ordered smectic mesophase in compounds **21-24**. Further, an increase in terminal alkyl chain dilutes the order leading to less ordered nematic mesophase which is proved in the next set of compounds.

In the fourth set of compounds **28-34**, having methylene spacer length: n = 12 and terminal alkyl chain length varying from n = 6-18, all the compounds **28-34** show two crystal-crystal transitions in both heating and cooling scans as Cr_1-Cr_2-I and reverse transition as I-N-Cr_2-Cr_1 respectively. Only two compounds **28** and **29** exhibit typical focal conic texture of SmA LC property with similar textural observations. Compound **29** heated to its isotropic state with Cr_1 at 84.6 °C (ΔH = 28.10) and Cr_2-I at 147.4 °C (ΔH = 33.20) transitions. While in the cooling cycle I-SmA at 116.5 °C (ΔH = -3.78), Smectic-Cr_2 at 93.9 °C (ΔH = -15.64) and then Cr_2-Cr_1 at 73.2 °C (ΔH = -52.18) transitions respectively, whereas compounds **30-33** shows a nematic phase. An optical photomicrograph of compound **33** exhibiting nematic mosaic texture upon cooling at 126 °C is depicted in Figure 2 (d). The last compound **34** did not show any LC

property. DSC thermograms as in Figure 1 (d) of compound **34** show two endothermic transitions at 128.2°C (ΔH =15.20) and 174.8 °C (ΔH = 17.52) with respect to Cr_1-Cr_2-I transitions. While in cooling scan, two exothermic transitions appeared at 96.3 °C (ΔH = -24.89) and 138.8 °C (ΔH = -19.33) for I-Cr_2 and Cr_2-Cr_1 respectively. The enthalpy values of I-Cr_2 (ΔH = -19.33) and Cr_2-Cr_1 (ΔH = -24.89) confirms the non-appearance of the mesophase in compound **34**.

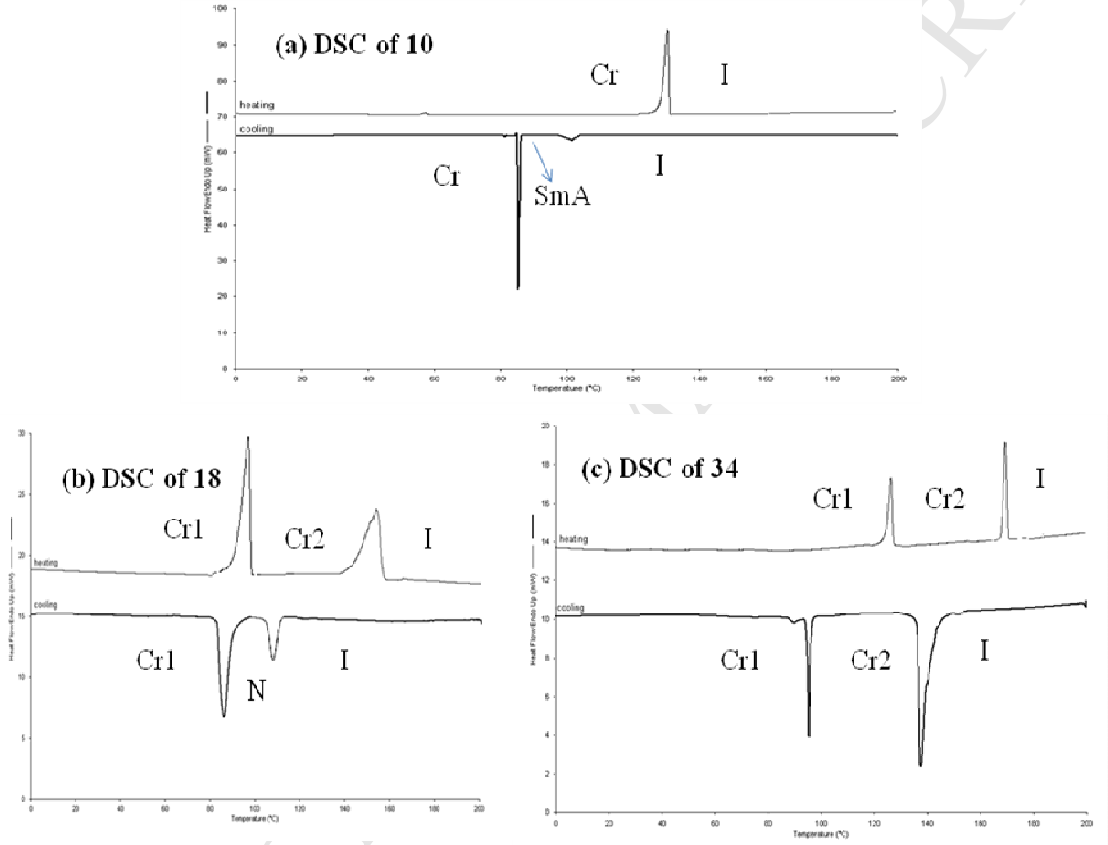


Figure 1. DSC thermograms of compounds (a) for **10**, (b) for **18** and (c) for **34**.

It was noted that in the cooling processes, enthalpy values are much lower than those during heating process (Table 1). This was generally encountered in the case of monotropic mesophases due to partial vitrification of the samples resulting from the slow kinetics of crystallization.[35] In our case, similar phenomena may be attributed to the slow kinetics of re-crystallization. However, the clearing points during cooling are much lower than that in the heating cycle, which may be due to the weak interactions among the LC molecules.

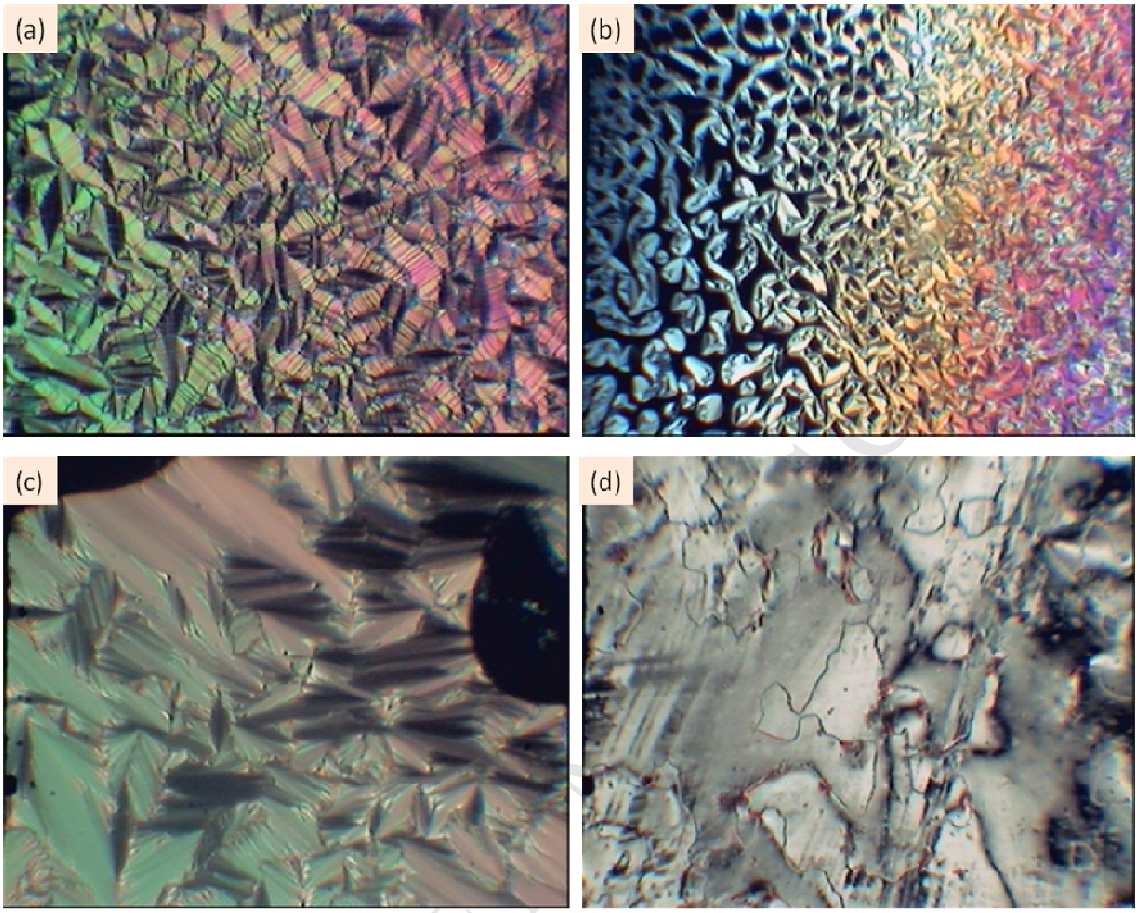


Figure 2. (a) Optical photomicrograph of compound **9** exhibiting SmA upon cooling at 95 °C (b) Optical photomicrograph of compound **12** upon cooling displaying SmA at 106 °C (c) Optical photomicrograph of compound **15** displaying SmA phase upon cooling at 109 °C. (d) Optical photomicrograph of compound **33** exhibiting nematic texture upon cooling at 126 °C.

The different mesophases were found for lower members (n = 6, 8 and 10) and higher members (n = 12, 14, 16 and 18) and can be explained by the number of aliphatic chains present at the periphery and at spacer position of the molecules. In this regard, a smaller aliphatic chain seems to be co-ordinating in terms of achieving a good packing with less random orientation of the molecules which may lead to a SmA mesophase. In the case of higher members the peripheral and spacer alkyl chains do not allow molecules to packing each other due to the bulky oxazepine heterocycle, and the disturbance may lead to exhibit the nematic phase. Appearance of a nematic mesophase in higher alkyl chains may be due to the increase in random orientations of

the molecule and least van der Waals attractive forces between the terminal and spacer alkyl chains.

The phase behaviour shown by the present four set of compounds is unusual. The conventional behaviour in liquid crystal dimers is smectic behaviour to be favoured on increasing the spacer length. Since in the present series of compunds nematic phase/non-liquid crystallinity is favoured in higher methylene spacer containing members, this behaviour is unexpected.[36]

A plot of transition temperature as a function of terminal/spacer chain length for the four sets of compounds **7-34** is shown in Figure 3. Figure 3(a) corresponds to compounds **7-13**, Figure 3(b) corresponds to compounds for **14-20**. Figure 3(c) corresponds to compounds **21-27**, and Figure 3(d) corresponds to compounds **28-34**. Figure 3 indicates that the mesophase ranges of compounds **7-13** and **14-20** are better than compounds **21-27** and **28-34**. In general, we observed in our target compounds **7-34**, the crystal to isotropic temperatures are high for lower members, low for middle members and again high for higher members. The temperature decreases in the beginning set of compounds, then increases with the increasing number of carbons in the methylene spacer and terminal alkyl chains. This behaviour suggests that increasing the carbon atoms in the methylene spacer serves to dilute the core-core interactions when compared with the terminal alkyl chain having six carbons. The enhancement nematic phase was formed when n = 10 and 12, indicating the order parameter is lost due to long alkyl chains.

The blunt end and relatively large size of the oxazepine heterocycle dimers result in high transition temperatures. To overcome that, we have extended the length of the spacer and terminal alkyl chains to attain low temperatures. This strategy works well in the reduction of transition temperature as we can observe in the plots of Figure 3.

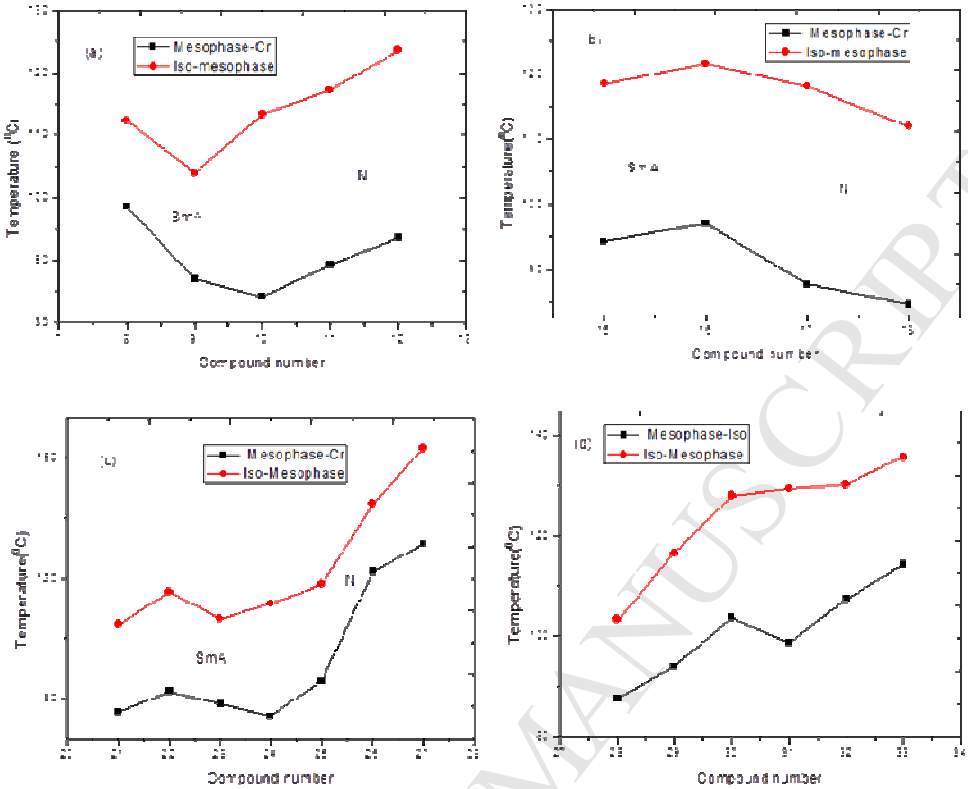


Figure 3. Plot of monotropic LC transition temperatures verses number of carbon atoms in the central connecting spaces and terminal alkyl chains: (a) for compounds **8-12**, (b) for compounds **15-18**, (c) for compounds **21-27** and (d) for compounds **28-33.**

Generally, in dimeric compounds, transition temperatures follow a pronounced odd-even effect, meaning odd number spacer molecules have low melting transition temperatures and even number spacer molecules have high melting transition temperatures. This behaviour is most commonly attributed to the pronounced dependence on the molecular shape, length and parity of the spacer.[37] Such behavior has been accounted for by theory, by means of the different shapes of the conformers having odd or even membered spacers, and their associated conformational distributions. As a result in the present series of oxazepine dimers the odd-even effect is eliminated.[38]

3. Conclusions

In this work we report that oxazepine heterocycle derived dimeric molecules can exhibit a good range of SmA and nematic mesophases with respect to their middle spacer and terminal alkyl chain length. We have also found rich polymorphism in most of the compounds, such as crystal-crystal (Cr_1-Cr_2), SmA and nematic phases. The mesophase formed in most of the compounds in the cooling process means that the mesophase is monotropic which was deduced by the comparison of DSC and POM results. Even though the molecules belong to a heterocyclic family, the transition temperatures are quite moderate instead of considerably high transition temperatures. When the terminal and spacer alkyl chain length increases, the nematic mesophase was favored due to reduction in the order parameter.

4. Experimental

4.1 Chemicals

The series of α,ω-dibromoalkanes, 4-hydroxybenzaldehyde, hexylamine, octylamine, decylamine, dodecylamine and phthalic anhydride were purchased from Sigma-Aldrich. Tetradecylamine, hexadecylamine and octadecylamine were procured from Acros Organics. The chemicals were used directly without further purification. Thin-layer chromatography (TLC) was performed on pre-coated silica-gel on aluminium plates.

4. 2 Instruments

Elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer. The molecular structure of intermediate and title compounds thus obtained were characterized using spectroscopic techniques. Fourier transform-infrared (FT-IR) spectra in the range of 4000-400 cm^{-1} was recorded using a Perkin Elmer 2000 FT-IR spectrophotometer and ^{1}H-NMR recorded using a Bruker 400MHz Ultrashield^{TM} spectrometer by dissolving compounds **1a-g, 2a-e** to **5a-e** in $CDCl_3$, while the title compounds **7-34** were dissolved in DMSO with tetramethylsilane (TMS) as the internal standard.

4. 3 General procedure for the synthesis of compounds **7-34**

The representative synthetic procedure is described here for compound **7**. The same procedure has been followed for the remaining target compounds **8-34**.

4-Hydroxybenzaldehyde was reacted with various amines (n = 6-18) to get intermediates **1a-g** and then reacted with series of dibromoalkanes (n = 6-12) to get **2a-e** to **5a-e** in moderate yields. Compound **2a** (492 mg, 1 mol) was reacted with phthalic anhydride **6** (296 mg, 2 mol) under reflux conditions in dry benzene at 80 ºC for 1 h. The reaction was monitored by TLC and the solvent was removed by distillation under reduced pressure. The solid product **7** thus obtained was filtered and recrystallized in absolute ethanol to obtain analytical pure compound. The analytical data of FT-IR, ^{1}H and ^{13}C NMR for compounds **7-34** are summarized as follows:

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (7)

Off white solid; (Yield: 441 mg, 56 %); IR: υ_{max}(KBr, cm^{-1}): 3007, 2944, 2870, 1660, 1600, 1588, 1266. ^{1}HNMR δ (ppm, DMSO): 9.80 (s, 2H, N-C<u>H</u>-Ar), 7.10 (d, 4H, *J* 8.5 Hz, Ar-<u>H</u>), 7.31 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.36 (d, 2H, *J* 8.1Hz, Ar-<u>H</u>), 7.81 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.95 (t, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.56 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 4.08 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.80 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.31-1.94 (m, 24H, -OCH$_2$-C<u>H</u>$_2$-), 0.95 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 168.70, 169.57 (C=O), 115.40-134.30 (Ar-C), 159.24 (Ar-C-O), 90.70 (C-N), 39.45 (N-CH$_2$), 22.12 (CH$_2$), 15.21 (CH$_3$) ppm. Elemental analysis found for $C_{48}H_{56}N_2O_8$ (%): C 73.20, H 7.02, N 3.31. Calc (%),C 73.07, H 7.15, N 3.55.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (8)

Off white solid; (Yield: 465 mg, 55 %); IR: υ_{max}(KBr, cm^{-1}): 3004, 2940, 2873, 1666, 1601, 1588, 1261. ^{1}HNMR δ (ppm, DMSO): 9.81 (s, 2H, N-C<u>H</u>-Ar), 7.10 (d, 4H, *J* 8.5 Hz, Ar-<u>H</u>), 7.33 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.34 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.80 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.93 (t, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.54 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.05 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.85 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.34-1.97 (m, 32H, -OCH$_2$-C<u>H</u>$_2$-), 0.96 (t, 6H, *J* 6.8 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 168.21, 169.47 (C=O), 115.01-134.57 (Ar-C), 159.90 (Ar-C-O), 90.58 (C-N), 39.17 (N-CH$_2$), 22.50 (CH$_2$), 15.00 (CH$_3$) ppm. Elemental analysis found for $C_{52}H_{64}N_2O_8$ (%): C 73.80, H 7.75, N 3.22. Calc (%), C 73.91, H 7.63, N 3.31 O.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-decyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (9)

Off white solid; (Yield: 543 mg, 60 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2956, 2887, 1667, 1600, 1584, 1261. ^{1}HNMR δ (ppm, DMSO): 9.84 (s, 2H, N-C<u>H</u>-Ar), 7.13 (d, 4H, *J* 8.6 Hz, Ar-<u>H</u>), 7.36 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.35 (d, 2H, *J* 8.3 Hz, Ar-<u>H</u>), 7.81 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.91 (t, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.51 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 4.01 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.84 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.37-1.98 (m, 40H, -OCH$_2$-C<u>H</u>$_2$-), 0.98 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 167.89, 169.00 (C=O), 116.23-134.92 (Ar-C), 160.07 (Ar-C-O), 90.45 (C-N), 39.10 (N-CH$_2$), 22.88 (CH$_2$), 14.67 (CH$_3$) ppm. Elemental analysis found for $C_{56}H_{72}N_2O_8$ (%):C 74.50, H 8.19, N 3.22. Calc (%), C 74.64, H 8.05, N 3.11.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-dodecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (10)

Off white solid; (Yield: 596 mg, 62 %); IR: υ_{max}(KBr, cm^{-1}): 3009, 2961, 2889, 1660, 1604, 1589, 1259. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-C<u>H</u>-Ar), 7.16 (d, 4H, *J* 8.5 Hz, Ar-<u>H</u>), 7.37 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.34 (d, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.84 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.90 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.53 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 4.07 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.87 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.35-1.93 (m, 48H, -OCH$_2$-C<u>H</u>$_2$-), 0.96 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.43, 168.87 (C=O), 115.02-134.27 (Ar-C), 160.41 (Ar-C-O), 90.06 (C-N), 39.21 (N-CH$_2$), 21.24 (CH$_2$), 14.88 (CH$_3$) ppm. Elemental analysis found $C_{60}H_{80}N_2O_8$ (%): C 75.07, H 8.60, N 2.81. Calc (%), C 75.28, H 8.42, N 2.93.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-tetradecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (11)

Off white solid; (Yield: 673 mg, 66 %); IR: υ_{max}(KBr, cm^{-1}): 3015, 2952, 2880, 1663, 1602, 1585, 1255. ^{1}HNMR δ (ppm, DMSO): 9.90 (s, 2H, N-C<u>H</u>-Ar), 7.13 (d, 4H, *J* 8.6 Hz, Ar-<u>H</u>), 7.33 (d, 4H, *J* 8.3 Hz, Ar-<u>H</u>), 8.38 (d, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.80 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.96 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.56 (d, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 4.04 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.81 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.38-1.96 (m, 56H, -OCH$_2$-C<u>H</u>$_2$-), 0.99 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.88, 167.94 (C=O), 116.34-134.00 (Ar-C), 160.23 (Ar-C-O), 90.22 (C-N), 39.04 (N-

CH_2), 22.56 (CH_2), 15.13 (CH_3) ppm. Elemental analysis found $C_{64}H_{88}N_2O_8$ (%): C 75.98, H 8.85, N 2.90. Calc (%), C 75.85, H 8.75, N 2.76.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (12)

Off white solid; (Yield: 646 mg, 60 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2969, 2872, 1668, 1603, 1580, 1252. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-C<u>H</u>-Ar), 7.11 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.36 (d, 4H, *J* 8.3 Hz, Ar-<u>H</u>), 8.35 (d, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.85 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.94 (t, 2H, *J* 8.2Hz, Ar-<u>H</u>), 7.50 (d, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 4.06 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.84 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.33-1.92 (m, 64H, -OCH$_2$-C<u>H</u>$_2$-), 0.90 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 165.20, 167.14 (C=O), 115.52-134.20 (Ar-C), 159.78 (Ar-C-O), 90.68 (C-N), 39.46 (N-CH_2), 21.20 (CH_2), 15.80 (CH_3) ppm. Elemental analysis found $C_{68}H_{96}N_2O_8$ (%): C 76.21, H 9.19, N 2.50. Calc (%), C 76.37, H 9.05, N 2.62.

1,6-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]hexane (13)

Off white solid; (Yield: 806 mg, 71 %); IR: υ_{max}(KBr, cm^{-1}): 3005, 2960, 2876, 1669, 1601, 1584, 1251. ^{1}HNMR δ (ppm, DMSO): 9.81 (s, 2H, N-C<u>H</u>-Ar), 7.16 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.38 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.36 (d, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.82 (t, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.92 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.56 (d, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 4.05 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.86 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.35-1.98 (m, 72H, -OCH$_2$-C<u>H</u>$_2$-), 0.94 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.82, 169.00 (C=O), 115.77-134.50 (Ar-C), 160.04 (Ar-C-O), 90.47 (C-N), 38.67 (N-CH_2), 22.69 (CH_2), 16.06 (CH_3) ppm. Elemental analysis found $C_{72}H_{104}N_2O_8$ (%): C 76.70, H 9.46, N 2.32. Calc (%), C 76.83, H 9.31, N 2.49.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (14)

Off white solid; (Yield 416 mg, 51 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2949, 2878, 1667, 1604, 1580, 1253. ^{1}HNMR δ (ppm, DMSO): 9.83 (s, 2H, N-C<u>H</u>-Ar), 7.12 (d, 4H, *J* 8.6 Hz, Ar-<u>H</u>), 7.35 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.32 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.84 (t, 2H, *J* 8.3 Hz, Ar-<u>H</u>), 7.92 (t, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.53 (d, 2H, *J* 8.3 Hz, Ar-<u>H</u>), 4.09 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.85 (t, 4H, *J* 4.1

Hz, -NC<u>H</u>$_2$-), 1.39-1.98 (m, 28H, -OCH$_2$-C<u>H</u>$_2$-), 0.99 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.04, 168.33 (C=O), 115.60-134.12 (Ar-C), 160.78 (Ar-C-O), 90.01 (C-N), 39.77 (N-CH$_2$), 22.88 (CH$_2$), 15.90 (CH$_3$) ppm. Elemental analysis found for $C_{50}H_{60}N_2O_8$ (%): C 73.32, H 7.59, N 3.49. Calc (%), C 73.50, H 7.40, N 3.43.

1,8-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (15)

Off white solid; (Yield: 480 mg, 55 %); IR: υ_{max}(KBr, cm^{-1}): 3007, 2950, 2872, 1664, 1601, 1583, 1260. ^{1}HNMR δ (ppm, DMSO): 9.82 (s, 2H, N-C<u>H</u>-Ar), 7.10 (d, 4H, *J* 8.6 Hz, Ar-<u>H</u>), 7.31 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.33 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 7.82 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.90 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.54 (d, 2H, *J* 8.7 Hz, Ar-<u>H</u>), 4.05 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.88 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.36-1.97 (m, 36H, -OCH$_2$-C<u>H</u>$_2$-), 0.93 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 164.62, 166.20 (C=O), 116.00-134.77 (Ar-C), 159.47 (Ar-C-O), 90.47 (C-N), 39.20 (N-CH$_2$), 21.37 (CH$_2$), 14.07 (CH$_3$) ppm. Elemental analysis found for $C_{54}H_{68}N_2O_8$ (%): C 74.14, H 7.72, N 3.32. Calc (%), C 74.28, H 7.85, N 3.21.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-decyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (16)

Off white solid; (Yield: 615 mg, 66 %); IR: υ_{max}(KBr, cm^{-1}): 3012, 2951, 2879, 1666, 1607, 1589, 1253. ^{1}HNMR δ (ppm, DMSO): 9.87 (s, 2H, N-C<u>H</u>-Ar), 7.13 (d, 4H, *J* 8.8 Hz, Ar-<u>H</u>), 7.37 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.38 (d, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.84 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.94 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.51 (d, 2H, *J* 8.7 Hz, Ar-<u>H</u>), 4.03 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.89 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.33-1.96 (m, 44H, -OCH$_2$-C<u>H</u>$_2$-), 0.98 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 165.33, 167.40 (C=O), 115.76-134.08 (Ar-C), 160.78 (Ar-C-O), 90.78 (C-N), 39.80 (N-CH$_2$), 22.66 (CH$_2$), 15.82 (CH$_3$) ppm. Elemental analysis found for $C_{58}H_{76}N_2O_8$ (%):C 74.82, H 8.12, N 3.20. Calc (%), C 74.97, H 8.24, N 3.01.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-dodecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (17)

Off white solid; (Yield: 732 mg, 74 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2961, 2880, 1661, 1603, 1583, 1262. ^{1}HNMR δ (ppm, DMSO): 9.85 (s, 2H, N-C<u>H</u>-Ar), 7.16 (d, 4H, *J* 8.8 Hz, Ar-<u>H</u>), 7.33

(d, 4H, *J* 8.2 Hz, Ar-H), 8.32 (d, 2H, *J* 8.7 Hz, Ar-H), 7.88 (t, 2H, *J* 8.6 Hz, Ar-H), 7.93 (t, 2H, *J* 8.4 Hz, Ar-H), 7.58 (d, 2H, *J* 8.7 Hz, Ar-H), 4.08 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.84 (t, 4H, *J* 4.1Hz, -NCH_2-), 1.36-1.94 (m, 52H, -OCH_2-CH_2-), 0.99 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 166.43, 168.78 (C=O), 116.02-134.66 (Ar-C), 160.18 (Ar-C-O), 90.00 (C-N), 39.41 (N-CH_2), 21.48 (CH_2), 15.08 (CH_3) ppm. Elemental analysis found for $C_{62}H_{84}N_2O_8$ (%): C 75.41, H 8.72, N 2.93. Calc (%), C 75.57, H 8.59, N 2.84.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-tetradecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (18)

Off white solid; (Yield: 754 mg, 72 %); IR: υ_{max}(KBr, cm^{-1}): 3008, 2956, 2874, 1665, 1602, 1586, 1254. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-CH-Ar), 7.14 (d, 4H, *J* 8.8 Hz, Ar-H), 7.31 (d, 4H, *J* 8.2 Hz, Ar-H), 8.35 (d, 2H, *J* 8.7 Hz, Ar-H), 7.86 (t, 2H, *J* 8.6 Hz, Ar-H), 7.96 (t, 2H, *J* 8.4 Hz, Ar-H), 7.56 (d, 2H, *J* 8.7 Hz, Ar-H), 4.01 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.82 (t, 4H, *J* 4.1 Hz, -NCH_2-), 1.33-1.95 (m, 60H, -OCH_2-CH_2-), 0.94 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 166.67, 168.94 (C=O), 115.48-134.02 (Ar-C), 160.58 (Ar-C-O), 90.46 (C-N), 39.05 (N-CH_2), 22.43 (CH_2), 14.33 (CH_3) ppm. Elemental analysis found for $C_{66}H_{92}N_2O_8$ (%):C 76.28, H 8.78, N 2.54. Calc (%), C 76.12, H 8.90, N 2.69.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (19)

Off white solid; (Yield: 851 mg, 77 %); IR: υ_{max}(KBr, cm^{-1}): 3012, 2954, 2871, 1660, 1606, 1589, 1260. ^{1}HNMR δ (ppm, DMSO): 9.84 (s, 2H, N-CH-Ar), 7.10 (d, 4H, *J* 8.8 Hz, Ar-H), 7.34 (d, 4H, *J* 8.2 Hz, Ar-H), 8.32 (d, 2H, *J* 8.8 Hz, Ar-H), 7.81 (t, 2H, *J* 8.6 Hz, Ar-H), 7.92 (t, 2H, *J* 8.4 Hz, Ar-H), 7.54 (d, 2H, *J* 8.9 Hz, Ar-H), 4.06 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.86 (t, 4H, *J* 4.1 Hz, -NCH_2-), 1.34-1.98 (m, 68H, -OCH_2-CH_2-), 0.98 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 165.40, 167.60 (C=O), 115.08-134.48 (Ar-C), 159.87 (Ar-C-O), 89.70 (C-N), 39.46 (N-CH_2), 21.86 (CH_2), 15.88 (CH_3) ppm. Elemental analysis found for $C_{70}H_{100}N_2O_8$ (%): C 76.82, H 9.29, N 2.41. Calc (%),C 76.60, H 9.18, N 2.55.

1,8- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]octane (20)

Off white solid; (Yield: 860 mg, 74 %); IR: υ_{max}(KBr, cm^{-1}): 3018, 2960, 2881, 1664, 1602, 1583, 1262. ^{1}HNMR δ (ppm, DMSO): 9.89 (s, 2H, N-CH-Ar), 7.19 (d, 4H, *J* 8.7 Hz, Ar-H), 7.38 (d, 4H, *J* 8.3 Hz, Ar-H), 8.38 (d, 2H, *J* 8.6 Hz, Ar-H), 7.88 (t, 2H, *J* 8.6 Hz, Ar-H), 7.95 (t, 2H, *J* 8.4 Hz, Ar-H), 7.57 (d, 2H, *J* 8.9 Hz, Ar-H), 4.07 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.88 (t, 4H, *J* 4.1 Hz, -NCH_2-), 1.36-1.95 (m, 76H, -OCH_2-CH_2-), 0.94 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 166.08, 168.31 (C=O), 116.21-134.53 (Ar-C), 160.28 (Ar-C-O), 90.27 (C-N), 38.72 (N-CH_2), 22.17 (CH_2), 14.39 (CH_3) ppm. Elemental analysis found for $C_{74}H_{108}N_2O_8$ (%): C 77.28, H 9.31, N 2.52. Calc (%),C 77.04, H 9.44, N 2.43.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (21)

White solid; (Yield: 439 mg, 52 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2950, 2873 1664, 1602, 1580, 1262. ^{1}HNMR δ (ppm, DMSO): 9.83 (s, 2H, N-CH-Ar), 7.14 (d, 4H, *J* 8.7 Hz, Ar-H), 7.33 (d, 4H, *J* 8.3 Hz, Ar-H), 8.34 (d, 2H, *J* 8.2 Hz, Ar-H), 7.80 (t, 2H, *J* 8.6 Hz Ar-H), 7.92 (t, 2H, *J* 8.4 Hz, Ar-H), 7.52 (d, 2H, *J* 8.1 Hz, Ar-H), 4.00 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.82 (t, 4H, *J* 4.1Hz, - NCH_2-), 1.36-1.98 (m, 32H, -OCH_2-CH_2-), 0.99 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 165.24, 167.08 (C=O), 116.11-134.68 (Ar-C), 160.67 (Ar-C-O), 89.40 (C-N), 39.07 (N-CH_2), 21.90 (CH_2), 15.68 (CH_3) ppm. Elemental analysis found for $C_{52}H_{64}N_2O_8$ (%): C 73.80, H 7.54, N 3.43. Calc (%),C 73.91, H 7.63, N 3.31.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (22)

White solid; (Yield: 559 mg, 62 %); IR: υ_{max}(KBr, cm^{-1}): 3005, 2956, 2871 1661, 1600, 1583, 1260. ^{1}HNMR δ (ppm, DMSO): 9.86 (s, 2H, N-CH-Ar), 7.11 (d, 4H, *J* 8.7 Hz, Ar-H), 7.38 (d, 4H, *J* 8.4 Hz, Ar-H), 8.30 (d, 2H, *J* 8.2 Hz, Ar-H), 7.86 (t, 2H, *J* 8.6 Hz, Ar-H), 7.90 (t, 2H, *J* 8.4 Hz, Ar-H), 7.57 (d, 2H, *J* 8.1 Hz, Ar-H), 4.06 (t, 4H, *J* 6.4 Hz, -OCH_2-), 3.80 (t, 4H, *J* 4.1 Hz, -NCH_2-), 1.33-1.95 (m, 40H, -OCH_2-CH_2-), 0.94 (t, 6H, *J* 6.7 Hz, -CH_3). ^{13}C NMR δ (ppm): 166.42, 168.26 (C=O), 116.58-134.08 (Ar-C), 160.31 (Ar-C-O), 89.90 (C-N), 39.56 (N-CH_2), 22.67 (CH_2), 14.05 (CH_3) ppm. Elemental analysis found for $C_{56}H_{72}N_2O_8$ (%): C 74.81, H 8.20, N 3.03. Calc (%), C 74.64, H 8.05, N 3.11.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-decyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (23)

White solid; (Yield: 943 mg, 67 %); IR: υ_{max}(KBr, cm^{-1}): 3011, 2960, 2878 1668, 1604, 1588, 1254. ^{1}HNMR δ (ppm, DMSO): 9.82 (s, 2H, N-C<u>H</u>-Ar), 7.19 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.36 (d, 4H, *J* 8.4 Hz, Ar-<u>H</u>), 8.38 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.89 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.96 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.56 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.03 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.88 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.39-1.98 (m, 48H, -OCH$_2$-C<u>H</u>$_2$-), 0.97 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.27, 168.70 (C=O), 115.58-134.31 (Ar-C), 159.79 (Ar-C-O), 90.24 (C-N), 39.15 (N-CH_2), 21.00 (CH_2), 14.60 (CH_3) ppm. Elemental analysis found for $C_{60}H_{80}N_2O_8$ (%): C 75.13, H 8.57, N 2.81. Calc (%), C 75.28, H 8.42, N 2.93.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-dodecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (24)

White solid; (Yield: 748 mg, 77 %); IR: υ_{max}(KBr, cm^{-1}): 3014, 2958, 2872 1660, 1602, 1584, 1251. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-C<u>H</u>-Ar), 7.17 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.39 (d, 4H, *J* 8.3 Hz, Ar-<u>H</u>), 8.32 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.88 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.98 (t, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.52 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.08 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.86 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.38-1.96 (m, 56H, -OCH$_2$-C<u>H</u>$_2$-), 0.93 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 165.00, 167.29 (C=O), 116.20-133.87 (Ar-C), 160.25 (Ar-C-O), 90.68 (C-N), 38.70 (N-CH_2), 22.24 (CH_2), 15.07 (CH_3) ppm. Elemental analysis found for $C_{64}H_{88}N_2O_8$ (%): C 75.69, H 8.84, N 2.70. Calc (%), C 75.85, H 8.75, N 2.76.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-tetradecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (25)

White solid; (Yield: 824 mg, 76 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2953, 2878 1669, 1605, 1588, 1263. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-C<u>H</u>-Ar), 7.12 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.33 (d, 4H, *J* 8.4 Hz, Ar-<u>H</u>), 8.38 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.82 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.95 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.51 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.02 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.87 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.35-1.94 (m, 64H, -OCH$_2$-C<u>H</u>$_2$-), 0.90 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 165.48, 167.05 (C=O), 115.18-134.35 (Ar-C), 160.05 (Ar-C-O), 90.92 (C-N), 38.46 (N-CH_2),

22.80 (CH_2), 15.14 (CH_3) ppm. Elemental analysis found for $C_{68}H_{96}N_2O_8$ (%): C 76.53, H 9.23, N 2.68. Calc (%), C 76.37, H 9.05, N 2.62.

1,10-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (26)

White solid; (Yield: 850 mg, 75 %); IR: υ_{max}(KBr, cm^{-1}): 3019, 2960, 2873 1664, 1602, 1581, 1255. ^{1}HNMR δ (ppm, DMSO): 9.83 (s, 2H, N-C<u>H</u>-Ar), 7.16 (d, 4H, *J* 8.6 Hz, Ar-<u>H</u>), 7.36 (d, 4H, *J* 8.4 Hz, Ar-<u>H</u>), 8.33 (d, 2H, *J* 8.8 Hz, Ar-<u>H</u>), 7.80 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.98 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.54 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.05 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.87 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.37-1.99 (m, 72H, -OCH$_2$-C<u>H</u>$_2$-), 0.96 (t, 6H, *J* = 6.76 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.48, 169.21 (C=O), 116.31-134.89 (Ar-C), 160.24 (Ar-C-O), 90.42 (C-N), 39.33 (N-CH_2), 21.50 (CH_2), 14.27 (CH_3) ppm. Elemental analysis found for $C_{72}H_{104}N_2O$ (%): C 76.94, H 9.20, N 2.44. Calc (%),C 76.83, H 9.31, N 2.49.

1,10- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]decane (27)

White solid; (Yield: 930 mg, 78 %); IR: υ_{max}(KBr, cm^{-1}): 3012, 2959, 2878 1661, 1601, 1584, 1260. ^{1}HNMR δ (ppm, DMSO): 9.82 (s, 2H, N-C<u>H</u>-Ar), 7.12 (d, 4H, *J* 8.7 Hz, Ar-<u>H</u>), 7.31 (d, 4H, *J* 8.5 Hz, Ar-<u>H</u>), 8.30 (d, 2H, *J* 8.8 Hz, Ar-<u>H</u>), 7.82 (t, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.92 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.50 (d, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 4.07 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.88 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.34-1.97 (m, 80H, -OCH$_2$-C<u>H</u>$_2$-), 0.96 (t, 6H, *J* = 6.76 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.87, 168.70 (C=O), 115.01-134.20 (Ar-C), 160.58 (Ar-C-O), 90.20 (C-N), 39.69 (N-CH_2), 22.46 (CH_2), 15.38 (CH_3) ppm. Elemental analysis found for $C_{76}H_{112}N_2O_8$ (%): C 77.12, H 9.68, N 2.30. Calc (%), C 77.25, H 9.55, N 2.37.

1,12- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (28)

White solid; (Yield: 611 mg, 70 %); IR: υ_{max}(KBr, cm^{-1}): 3014, 2956, 2870 1670, 1601, 1589, 1255. ^{1}HNMR δ (ppm, DMSO): 9.82 (s, 2H, N-C<u>H</u>-Ar), 7.10 (d, 4H, *J* 8.9 Hz, Ar-<u>H</u>), 7.35 (d, 4H, *J* 8.2 Hz, Ar-<u>H</u>), 8.32 (d, 2H, *J* 8.3 Hz, Ar-<u>H</u>), 7.84 (t, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.91 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.57 (d, 2H, *J* 8.0 Hz, Ar-<u>H</u>), 4.04 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.85 (t, 4H, *J*

4.1Hz, -NC<u>H</u>$_2$-), 1.39-1.99 (m, 36H, -OCH$_2$-C<u>H</u>$_2$-), 0.91 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.71, 169.00 (C=O), 115.36-134.26 (Ar-C), 159.11 (Ar-C-O), 90.76 (C-N), 39.19 (N-CH$_2$), 22.83 (CH$_2$), 14.27 (CH$_3$) ppm. Elemental analysis found for $C_{54}H_{68}N_2O_8$ (%): C 74.40, H 7.66, N 3.15. Calc (%), C 74.28, H 7.85, N 3.21.

1,12- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (29)

White solid; (Yield: 633 mg, 68 %); IR: υ_{max}(KBr, cm^{-1}): 3012, 2950, 2879 1675, 1600, 1584, 1254. ^{1}HNMR δ (ppm, DMSO): 9.81 (s, 2H, N-C<u>H</u>-Ar), 7.10 (d, 4H, *J* 8.9 Hz, Ar-<u>H</u>), 7.32 (d, 4H, *J* 8.3 Hz, Ar-<u>H</u>), 8.39 (d, 2H, *J* 8.4 Hz, Ar-<u>H</u>), 7.82 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.96 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.58 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.01 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.88 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.37-1.96 (m, 44H, -OCH$_2$-C<u>H</u>$_2$-), 0.97 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 165.90, 167.33 (C=O), 116.41-134.63 (Ar-C), 160.40 (Ar-C-O), 90.76 (C-N), 38.33 (N-CH$_2$), 21.00 (CH$_2$), 14.88 (CH$_3$) ppm. Elemental analysis found for $C_{58}H_{76}N_2O_8$ (%):C 74.86, H 8.17, N 3.09. Calc (%), C 74.97, H 8.24, N 3.01.

1,12-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-decyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (30)

White solid; (Yield: 603 mg, 61 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2956, 2878 1673, 1603, 1580, 1261. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-C<u>H</u>-Ar), 7.16 (d, 4H, *J* 8.8 Hz, Ar-<u>H</u>), 7.36 (d, 4H, *J* 8.4 Hz, Ar-<u>H</u>), 8.36 (d, 2H, *J* 8.5 Hz, Ar-<u>H</u>), 7.84 (t, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.94 (t, 2H, *J* 8.3 Hz, Ar-<u>H</u>), 7.53 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.08 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.84 (t, 4H, *J* 4.1 Hz, -NC<u>H</u>$_2$-), 1.36-1.98 (m, 52H, -OCH$_2$-C<u>H</u>$_2$-), 0.99 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 164.16, 166.40 (C=O), 115.01-134.19 (Ar-C), 160.68 (Ar-C-O), 90.14 (C-N), 38.81 (N-CH$_2$), 22.33 (CH$_2$), 14.79 (CH$_3$) ppm. Elemental analysis found for $C_{62}H_{84}N_2O_8$ (%): C 75.39, H 8.64, N 2.78. Calc (%),C 75.57, H 8.59, N 2.84.

1,12-Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-dodecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (31)

White solid; (Yield: 753 mg, 72 %); IR: υ_{max}(KBr, cm^{-1}): 3005, 2952, 2872 1671, 1601, 1583, 1257. ^{1}HNMR δ (ppm, DMSO): 9.80 (s, 2H, N-C<u>H</u>-Ar), 7.13 (d, 4H, *J* 8.8 Hz, Ar-<u>H</u>), 7.34 (d,

4H, *J* 8.5 Hz, Ar-H), 8.32 (d, 2H, *J* 8.6 Hz, Ar-H), 7.82 (t, 2H, *J* 8.7 Hz, Ar-H), 7.96 (t, 2H, *J* 8.3 Hz, Ar-H), 7.52 (d, 2H, *J* 8.3 Hz, Ar-H), 4.00 (t, 4H, *J* 6.4 Hz, -OCH$_2$-), 3.81 (t, 4H, *J* 4.1 Hz, -NCH$_2$-), 1.33-1.96 (m, 60H, -OCH$_2$-CH$_2$-), 0.92 (t, 6H, *J* 6.7 Hz, -CH$_3$). ^{13}C NMR δ (ppm): 164.39, 166.75 (C=O), 115.61-134.57 (Ar-C), 160.03 (Ar-C-O), 89.63 (C-N), 38.16 (N-CH$_2$), 21.14 (CH$_2$), 14.96 (CH$_3$) ppm. Elemental analysis found for $C_{66}H_{92}N_2O_8$ (%): C 76.28, H 8.76, N 2.58. Calc (%), C 76.12, H 8.90, N 2.69.

1,12- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-tetradecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (32)

White solid; (Yield: 817 mg, 74 %); IR: υ_{max}(KBr, cm^{-1}): 3010, 2951, 2863 1668, 1603, 1584, 1262. ^{1}HNMR δ (ppm, DMSO): 9.88 (s, 2H, N-CH-Ar), 7.15 (d, 4H, *J* 8.8 Hz, Ar-H), 7.33 (d, 4H, *J* 8.5 Hz, Ar-H), 8.34 (d, 2H, *J* 8.6 Hz, Ar-H), 7.86 (t, 2H, *J* 8.6 Hz, Ar-H), 7.94 (t, 2H, *J* 8.3 Hz, Ar-H), 7.59 (d, 2H, *J* 8.1 Hz, Ar-H), 4.07 (t, 4H, *J* 6.4 Hz, -OCH$_2$-), 3.85 (t, 4H, *J* 4.1Hz, -NCH$_2$-), 1.37-1.99 (m, 68H, -OCH$_2$-CH$_2$-), 0.95 (t, 6H, *J* 6.7 Hz, -CH$_3$). ^{13}C NMR δ (ppm): 165.20, 167.14 (C=O), 116.39-134.07 (Ar-C), 159.67 (Ar-C-O), 90.03 (C-N), 38.55 (N-CH$_2$), 22.68 (CH$_2$), 14.00 (CH$_3$) ppm. Elemental analysis found for $C_{70}H_{100}N_2O_8$ (%): C 76.52, H 9.10, N 2.61. Calc (%), C 76.60, H 9.18, N 2.55.

1,12- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-hexadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (33)

White solid; (Yield: 848 mg, 73 %); IR: υ_{max}(KBr, cm^{-1}): 3019, 2954, 2860 1670, 1601, 1589, 1257. ^{1}HNMR δ (ppm, DMSO): 9.89 (s, 2H, N-CH-Ar), 7.17 (4H, d, *J* 8.8 Hz, Ar-H), 7.39 (4H, d, *J* 8.5 Hz, Ar-H), 8.38 (2H, d, *J* 8.5 Hz, Ar-H), 7.85 (2H, t, *J* 8.7 Hz, Ar-H), 7.90 (2H, t, *J* 8.3 Hz, Ar-H), 7.54 (2H, d, *J* 8.1 Hz, Ar-H), 4.07 (t, 4H, *J* 6.4 Hz, -OCH$_2$-), 3.89 (t, 4H, *J* 4.1Hz, -NCH$_2$-), 1.39-1.98 (m, 76H, -OCH$_2$-CH$_2$-), 0.98 (t, 6H, *J* 6.7 Hz, -CH$_3$). ^{13}C NMR δ (ppm): 166.36, 168.05 (C=O), 115.31-134.20 (Ar-C), 160.52 (Ar-C-O), 90.01 (C-N), 38.03 (N-CH$_2$), 21.25 (CH$_2$), 15.80 (CH$_3$) ppm. Elemental analysis found for $C_{74}H_{108}N_2O_8$ (%): C 77.18, H 9.32, N 2.40. Calc (%), C 77.04, H 9.44, N 2.43.

1,12- Bis[(1´-phenyloxy)- 4´-(3´´-(1´´,5´´-dioxo-4´´-octadecyl-1´´,3´´,4´´,5´´-tetrahydro-2´´,4´´-benzoxazepinyl))]dodecane (34)

White solid; (Yield: 853 mg, 70 %); IR: υ_{max}(KBr, cm^{-1}): 3009, 2958, 2853 1673, 1600, 1582, 1261. ^{1}HNMR δ (ppm, DMSO): 9.87 (s, 2H, N-C<u>H</u>-Ar), 7.11 (d, 4H, *J* 8.8 Hz, Ar-<u>H</u>), 7.33 (d, 4H, *J* 8.5 Hz, Ar-<u>H</u>), 8.34 (d, 2H, *J* 8.6 Hz, Ar-<u>H</u>), 7.80 (t, 2H, *J* 8.9 Hz, Ar-<u>H</u>), 7.94 (t, 2H, *J* 8.2 Hz, Ar-<u>H</u>), 7.58 (d, 2H, *J* 8.1 Hz, Ar-<u>H</u>), 4.09 (t, 4H, *J* 6.4 Hz, -OC<u>H</u>$_2$-), 3.84 (t, 4H, *J* 4.1Hz, -NC<u>H</u>$_2$-), 1.32-1.95 (m, 84H, -OCH$_2$-C<u>H</u>$_2$-), 0.99 (t, 6H, *J* 6.7 Hz, -C<u>H</u>$_3$). ^{13}C NMR δ (ppm): 166.07, 168.46 (C=O), 116.19-134.85 (Ar-C), 160.06 (Ar-C-O), 90.67 (C-N), 38.27 (N-CH_2), 22.08 (CH_2), 14.24 (CH_3) ppm. Elemental analysis found for $C_{78}H_{116}N_2O_8$ (%): C 77.44, H 9.66, N 2.32. Calc (%), C 77.49, H 9.73, N 2.38.

Acknowledgement

AK-T M extends grateful thanks to Prof. John West and Liquid Crystal Institute at the Kent State University, for performing molecular model calculations and their hospitality. Authors thank the University Sains Malaysia and the Malaysian Government for financing this project through the short term Grant (304/PKIMIA/6312051) and FRGS Grant (203/ PKIMIA/671119). Corresponding author thanks Department of Chemistry, College of Sciences, University of Anbar.

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