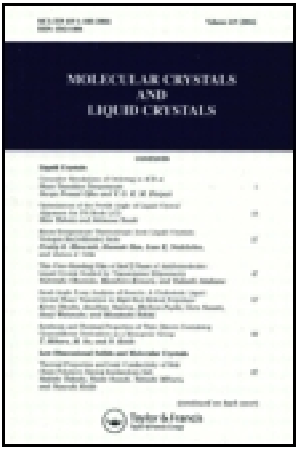

Molecular Crystals and Liquid Crystals

Monodispersive Unsymmetrical Tetramers Exhibiting a Columnar Phase

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MONODISPERSIVE UNSYMMETRICAL TETRAMERS EXHIBITING A COLUMNAR PHASE

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Oligomeric liquid crystals that are formed by joining two or more mesogenic segments axially through a flexible spacer (or multiple spacers) seem to be interesting materials from the points of view of both basic research and practical applications owing to their multifunctional characteristics and properties similar to those of polymers while retaining fluidity, viscosity etc. associated with those of low molar mass liquid crystals. The synthesis and evaluation of mesomorphic behavior of two novel monodispersive unsymmetrical tetramesogens have been presented here in detail. The molecular design of these tetramesogens incorporates the cholesteryl ester (as a chiral entity), biphenyl (as a supportive entity for mesomorphism), azobenzene (as a photoactive mesogen), and tolan (as a half-disc) segments interconnected through even-even-odd and odd-even-odd alkylene spacers. The target liquid crystalline tetramers have been realized by employing convenient synthetic strategies, which involves the preparation of two important unsymmetrical dimers and finally their condensation. The molecular structures of all the intermediates and unsymmetrical tetramers have been characterized by spectroscopic analyses. The mesomorphic property of both the unsymmetrical tetramers has been evaluated by optical microscopic, calorimetric and X-ray diffraction studies. Our study reveals that both oligomers show an identical mesophase. While X-ray studies suggest that the structure of the mesophase is similar to that of a rectangular columnar (Col_r) mesophase; a pseudoisotropic texture was seen under the microscope.

Keywords: oligomers; tetramers; multifunctions; synthesis; columnar phase

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INTRODUCTION

The formation of a thermotropic liquid crystalline phase is predominately caused by anisometric molecules, which have either a rod-shape [1] (calamitic) or a disc-shape [2] (discotic). By employing these two anisometric moieties many conventional low molar mass (monomers) as well as high molar mass (polymers) liquid crystalline systems have been designed and synthesized. The thermal behaviors of such monomeric and polymeric liquid crystals are well understood and consequently have been used as active media in display device technology [3]. They are also considered as potential candidates in applications involving information storage [4], nonlinear optics [5] and photoconductivity [6]. It is known that in both monomeric and polymeric liquid crystals (LCs), the shape of the anisometric entity determines the type of mesophase formed. Thus LCs with rod-like molecules exhibit nematic (N) and/or smectic (Sm) mesophases whereas LCs with flat disc-shaped and also cone-shaped [7] molecules organize to give N and/or columnar (Col) mesophases. Additionally, tapered or cone-shaped amphiphilic [8] or dendritic [9] systems are shown to self assemble into Col or micellar cubic (Cub) mesophases.

Recently, the design, synthesis and evaluation of the thermal behavior of new types of molecular structure which can be thought of as bridging the gap between calamitic and disc-shaped mesogens, has been the subject of numerous scientific publications [10–11]. One approach to realize these “non-conventional” LCs has been the synthesis of mesogens that combine the features of both types molecular geometries in which rod-like and disc-like (or rather half-disc type) entities are covalently attached to each other through the functional linkage. The examples of this type of LCs are the polycatenars [10b], in which the central rod-like rigid core is connected to the two terminal half disc-shaped moieties through an ester or an imine linkage. Many polycatenars have been reported and interestingly some of the tetracatenar, especially the biforked type, mesogens have indeed exhibited both lamellar and Col phases in addition to the Cub and N mesophases [10e,h,i].

An alternative approach in this direction has been to link the anisometric entities through flexible spacers [12–15]. Here again two different routes have been followed yielding oligomeric liquid crystals (OLCs). One way is to connect the different mesogenic segments around a certain central unit [12]. The second route is to join the mesogenic segments in an end-end (axial) fashion by means of polymethylene or a oligo(oxyethylene) or a oligosiloxyl group. The latter type of materials which we refer to as linear OLCs is attracting special attention not only because they are considered as model compounds for polymeric liquid crystals but also due to their unique thermal behavior [13–15]. Most importantly, OLCs can exhibit properties usually associated with polymers, while still retaining the fluidity and viscosity of a low molar mass LC. The transitional properties of such OLCs shows a dramatic dependence on the length and parity of the flexible spacer. This is most often attributed to the dependence of the molecular shape on the parity of the spacer considered in the all-trans conformation. Further, if the OLC is monodisperse it will lead to rather well defined properties unlike in polymers.

Of all the linear oligomeric molecular architectures known to support liquid crystalline behavior, the first member, namely the dimer (also referred to as dimesogen) composed of either identical (symmetrical) or non-identical (unsymmetrical) mesogenic segments connected by a central spacer has been extensively studied [13] in their own right because they exhibit quite different behavior to conventional low molar mass liquid crystals containing just a single mesogenic unit.

The addition of one to six mesogenic moieties to a dimer via a flexible spacer results in the next higher oligomers which have been called in general as a trimer, tetramer, pentamer, hexamer, heptamer and octamers respectively. Based on the molecular structure of the individual mesogenic segments, there can be three combinations: (i) symmetrical OLCs where all the segments are structurally similar (ii) partially identical OLCs in which some of segments are identical and (iii) unsymmetrical OLCs where no two segments are identical.

Trimers of types (i) and (ii) were reported for the first time in 1986 and since then a few other examples have been reported [14a–f]. Recently, there have been two reports [14g–i], including one from our laboratory [14i] of the first examples of trimers of type (iii). The unsymmetrical trimer that we synthesized consists of three different calamitic mesogenic entities connected by paraffinic spacers. The motivation behind the molecular design of this molecule was to realize a multifunctional OLC which could perhaps replace mixtures of mesogenic compounds, which have been used in different applications, thereby solving phase separation problems associated with such mixtures [16]. Interestingly this oligomer stabilizes a recently discovered highly frustrated phase viz., undulated twist grain boundary (UTGB$_{C*}$)phase over a wide temperature range of 90°C.

A type (i) tetramer was first reported by Keller *et al.* in 1985 but this material was not mesogenic [15a]. Later in 1989 Griffin's group reported a series of tetrameric monodisperse model compounds chemically related to known main chain liquid crystalline polymers; interestingly all of them were found to be mesogenic [15c]. It was only recently that Imrie *et al.* extended this approach to furnish the first examples of the type (ii) tetramers [15d,e]. To the best of our knowledge the unsymmetrical tetramers consisting of four non-identical mesogenic segments connected linearly [type (iii)] have not been reported till now.

This prompted us to set our goal to design and synthesize OLC that (i) has chiral, thermochromic and photochromic segments, (ii) can possibly bridge the gap between rod-like and disc-like LCs and also (iii) bridge the gap between low molar mass LCs and polymers and thus furnish the first liquid crystalline unsymmetric tetramer composed of four structurally different mesogenic entities [21]. To meet the first criterion, the cholesterol moiety was chosen to be the chiral segment because it is a naturally occurring commercial product with a rigid structure possessing multiple chiral centers but on derivatization to its esters namely cholesteryl esters it exhibits LC phases [1]. Recently it has been shown that the combination of the cholesteryl ester unit with a tolan (diarylacetylene) [13e] or biphenyl unit [13f] via polymethylene spacer furnishes dimers exhibiting a chiral nematic (N*) mesophase known for thermochromic properties (temperature dependent wavelength of selective reflection) [17]. The linking of the cholesteryl ester entity with a biphenyl unit through a paraffinic spacer accounts for two mesogenic segments of the tetramer and is anticipated to impart the thermochromic functionality to it.

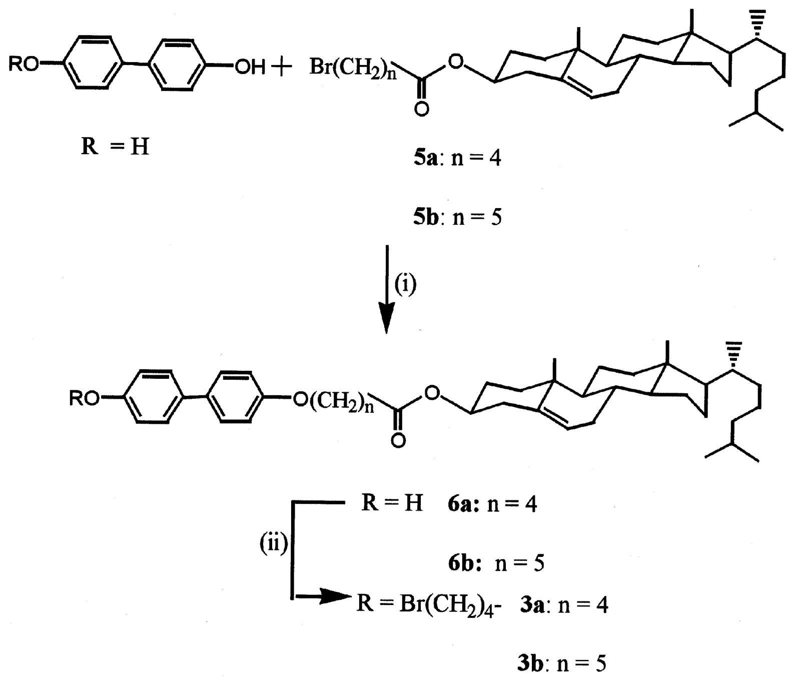
Azobenzene derivatives with appropriate substitutions exhibit mesomorphic properties. Upon irradiation with UV light the azo chromophore undergoes *cis* and t*rans* isomerism (photochromism) and the resulting photoinduced phenomenon is promising for many practical applications [18]. To incorporate a molecular segment with photochromic functionality we included an azobenzene moiety which links to other mesogenic segments through the spacer.

As mentioned earlier, among the polycatenars, the tetracatenar especially the biforked, type mesogens exhibit a rich mesomorphism showing lamellar, Col Cub and N phases. To have such an attractive feature in the proposed tetramer we planned to incorporate a tetracatenar type of structure. A linear addition of several mesogenic moieties through spacers leads to a macromolecule that may generally have a high clearing temperature and suffers from solubility problem in most common organic solvents. These problems are known to be solved by a lateral substitution. Therefore the fourth mesogenic entity needs to be like a semi-biforked entity having a lateral alkoxy substitution giving the segment the appearance of half-disc like structure. During our careful design we kept all these points in view, which led us to the synthesis of a new 2,3,4-trialkoxy substituted diphenylacetylene (tolan) segment that is used as the fourth mesogenic unit.

RESULTS AND DISCUSSION

Synthesis and Molecular Structural Characterization

In our present studies the molecular design incorporates the cholesteryl ester (as a chiral entity), biphenyl (as a supportive entity for thermochromism, azobenzene (as a photoactive mesogen), and tolan (as a half-disc) segments interconnected through even-even-odd (EEO) and odd-even-odd (OEO) paraffinic spacers. Such novel systems demand high yielding and convenient synthetic strategy. Here we present in detail the synthetic steps involved to realize the target liquid crystalline tetramers **1** and **2**. Schemes I, IIa,b,c and III, involve the preparation of two important unsymmetrical dimers **3a,b** and **4** and finally their condensation. Initially,

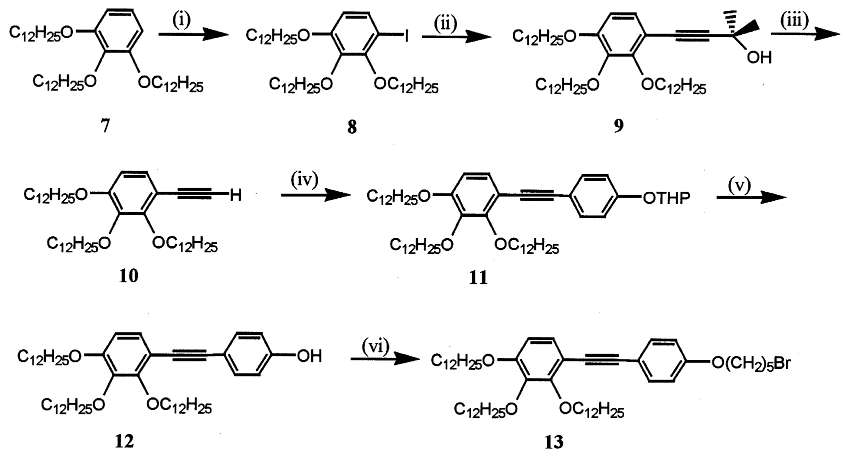


Reagents and conditions:

(i) anhyd.K_2CO_3, DMF, 85°C, 24hrs, 74 %.

(i) 1,4-Dibromobutane, anhyd.K_2CO_3, DMF, 85°C, 12hrs, 83 %

SCHEME I Synthesis of unsymmetrical dimers **3a** and **3b**.



Reagents and conditions:

(i) I_2-HIO_3, CH_3COOH, H_2SO_4, H_2O, rt, 18 hrs, 58 %

(ii) 2-Methyl-3-butyn-2-ol, $[(C_6H_5)_3P]_2PdCl_2$, CuI, Ph_3P, Et_3N, 65°C, 16hrs, 85 %

(iii) KOH, toluene, 110°C, 2hrs, 65 %

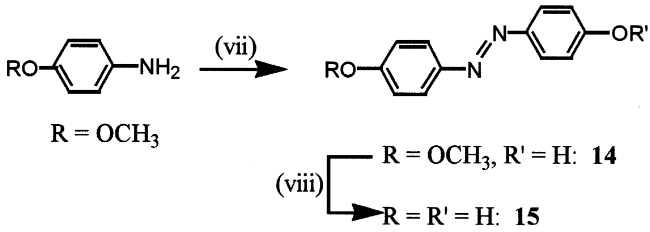
(iv) 4-Iodo-O-(tetrahydropyran-2-yl)phenol, $[(C_6H_5)_3P]_2PdCl_2$, CuI, Ph_3P, Et_3N, 65°C, 16hrs, 78 %

(v) PTSA, MeOH, THF, rt, 30min, 69 %

(vi) 1,5-Dibromopentane, anhyd.K_2CO_3, acetone, 50°C, 24hrs, quantitative

SCHEME IIA Synthesis of a half disc-shaped 2,3,4-trialkoxysubstituted diarylacetylene **13**.

cholesteryl bromoalkanoates **5a** and **5b** were obtained by esterification of commercial optically pure cholesterol with 5-bromopentanoyl and 6-bromohexanoyl chlorides respectively. These bromoesters were heated with

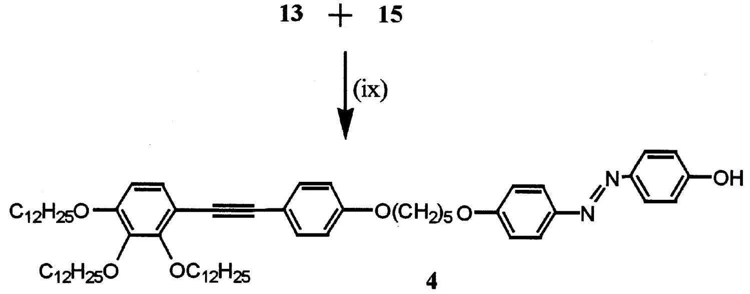


Reagents and conditions:

(vii) $NaNO_2$, HCl, phenol, 0-5°C 2hrs, 85 %

(viii) Pyridine, anhyd. $AlCl_3$, $CHCl_3$, reflux, 30hrs, 38 %

SCHEME IIB Synthesis of 4,4′-dihydroxyazobenzene **15**.



4

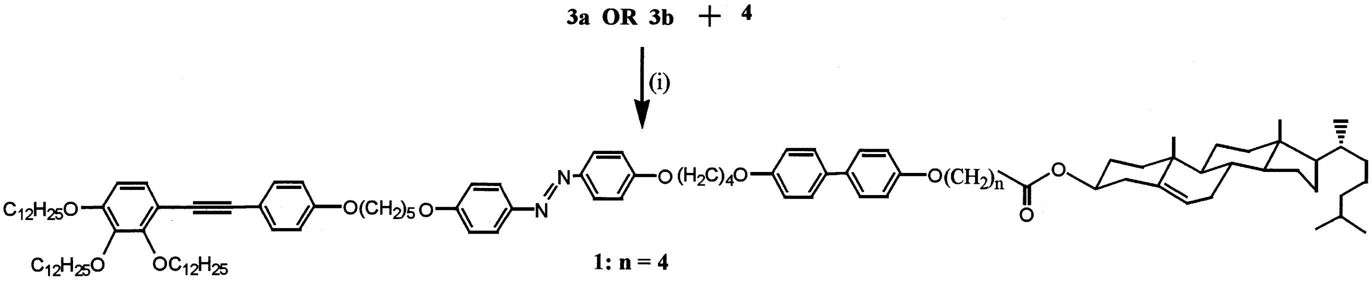
Reagents and conditions:

(ix) anhyd.K_2CO_3, DMF, 85°C, 30hrs, 40 %

SCHEME IIC Synthesis of an unsymmetrical dimer **4**.

4,4-dihydroxybiphenyl under mild basic reaction conditions to obtain unsymmetrical dimeric phenols [19] **6a** and **6b**, which upon treatment with 1,4-dibromobutane afforded dimers **3a** and **3b** carrying bromine atom substitution at terminal alkoxy chain (Scheme I).

A thermally stable half-disc shaped 2,3,4-trialkoxy substituted diarylacetylene (tolan) segment (**13**), which has not been reported previously, was prepared starting from 1,2,3-tridodecyloxybenzene (**7**). Firstly trialkoxy azobenzene was iodinated to get trialkoxy iodobenzene **8** which upon coupling with 2-methyl-3-butyn-2-ol under Hagihara-Sonogashira [20] reaction conditions to get protected phenylacetylene **9**. The deprotection of acetylene functionality by refluxing with potassium hydroxide in toluene furnished phenylacetylene **10** which was then coupled with THP-protected, 4-iodophenol to obtain diarylacetylene-THP ether **11**. Upon deprotection, the phenolic diarylacetylene **12** obtained was treated with 1,5-dibromopentane to get the half disc-shaped entity the tetracatenar **13,** in almost quantitative yield (Scheme IIa). 4,4-Dihydroxyazobenzene (**15**) was synthesized as shown in Scheme IIb. The coupling of diazonium salt of 4-methoxyaniline with phenol furnished 4-hydroxy-4′-methoxyazobenzene (**14**) which on treatment with aluminium trichloride/pyridine mixture in refluxing chloroform yielded compound **15**. The condensation of half equivalent of diarylacetylene **13** with azobenzene **15** finally gave the key dimeric intermediate **4** bearing terminal phenolic hydroxyl functionality (Scheme IIc). Optimization of the final coupling involving O-alkylation of dimeric phenol **4** with dimeric alkylbromide **3a** and **3b** to realize novel tetramer **1** and **2** finally proved that the presence of mild base (anhyd. potassium carbonate) in DMF, heating at 85°C for a period of 12 hrs is the superior condition than the others (Scheme III). Thus the tetramers **1** and **2** were obtained as a yellow powder in



1: n = 4

2: n = 5

Reagents and conditions:

(i) anhyd.K_2CO_3, DMF, 85°C, 12hrs, **1** : 49 % and **2** : 42 %

SCHEME III Synthesis of unsymmetrical liquid crystalline tetramers **1** and **2** containing four anisometric segments connected through even-even-odd and odd-even-odd paraffinic spacers respectively.

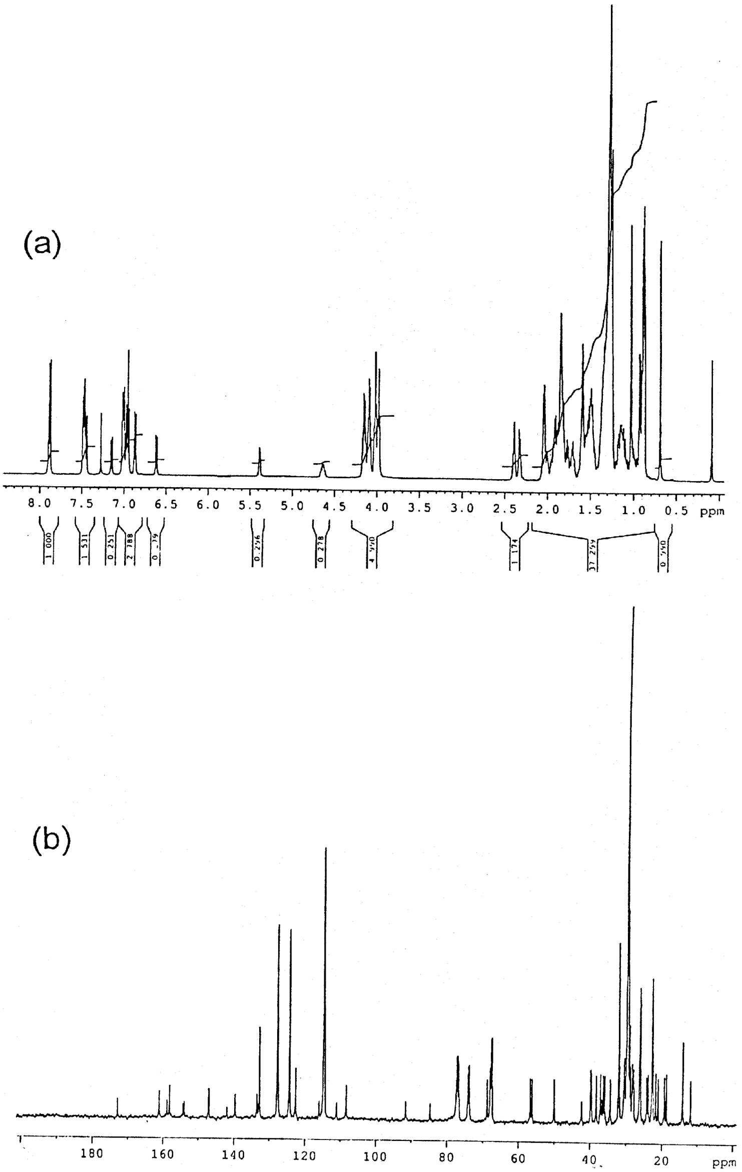


FIGURE 1 (a) and (b) show ^{1}H and ^{13}C NMR spectrum of the tetramer **1**.

49 and 42% yield respectively. The spectral data of all the intermediates and tetramers were confirmed by spectroscopic analysis. The IR, ^{1}H and ^{13}C NMR of both the Tetramers are comparable with each other. The IR spectrum

absorption bands in the region of υ_{max}/cm^{-1} 2923-2852 (C-H paraffinic), 1728–1737 (C=O stretching), 1581–1603 (C=C ring stretching). In the ^{1}H NMR spectrum 22 aromatic protons appear as eight doublets and one multiplet at δ 7.87, 7.13, 7.01, 6.98, 6.95, 6.936, 6.85, 6.60, and 7.46 respectively, while the olefinic, methine of (ester) and oxymethylene (of paraffinic chain) proton resonate at δ 5.37, 4.62, and 4.0 as broad d, multiplet(m) and triplet(t) respectively. In the ^{13}C NMR (SEFT; Spin Echo Fourier Transform) spectra at higher frequency region (downfield) tetramer **1** shows 24 peaks. As the expected number of peaks are 31, it indicates the equivalence of 7 sets of carbons (3 sets of quaternary and 4 sets of tertiary carbons are equivalent). Tetramer **2** shows 26 peaks, as the expected number of peaks are 31, it indicates the equivalence of 5 sets of carbons (1 set of quaternary and 4 sets of tertiary carbons are equivalent) (see experimental section for details and also). As a representative case ^{1}H and ^{13}C NMR of tetramer **1** have been presented in Figure 1.

THERMAL BEHAVIOR

Optical microscopic observations indicate that on melting at a temperature of 134.8°C for **1** and at 98.8°C for **2**, both the samples showed a pseudoisotropic texture. Figure 2a shows the pseudoisotropic texture seen for the tetramer **2** at about 150°C. This was true whether the substrate was a just a clean glass plate or a glass plate treated with either a polyimide solution for planar orientation or a silane solution for homeotropic alignment. On shearing the pseudoisotropic pattern changed to a birefringent texture, which almost immediately relaxed back into the pseudoisotropic texture in case of sample **1**. The birefringent pattern was like the sandy texture (Fig. 2b) usually observed in polymeric samples. Even at high magnification of microscope we could not get more details about the texture. This birefringent texture remained till the samples transformed to the isotropic phase at 191.2°C and 202.5°C for **1** and **2** respectively. On cooling from the isotropic phase, a slight supercooling was observed and the transition to the mesophase with the sandy texture was observed at 188.6°C (ΔH = 13.1 J/g) and 201.2°C (ΔH = 15.1 J/g) for **1** and **2** respectively. In case of the tetramer **1**, no other textural change was seen till crystallization, at 93°C. The differential scanning calorimetric (DSC) trace shown in Figure 3 (a: heating and b: cooling) corroborates these observations. These transitions are highly reproducible indicating the stability of this tetramer.

In sample **2**, while cooling, neither a textural change nor crystallization was seen till room temperature. The DSC traces shown in Figure 4 (b and c) support these optical observations. In addition it appears to show a

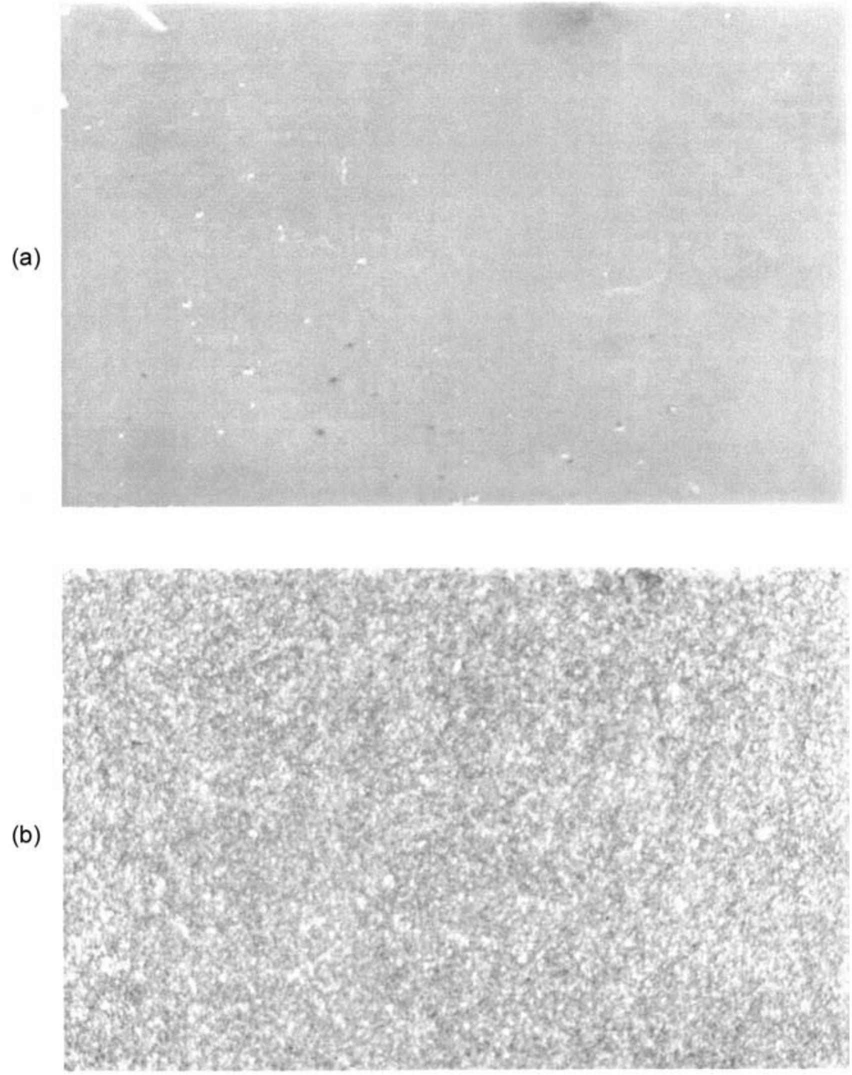


FIGURE 2 (a) Microphotograph of the pseudoisotropic texture seen for the tetramer **1** at 150°C, (b) sandy texture seen when pseudoisotropic texture subjected to shear. (See Color Plates XX & XXI).

glassy state [see inset (d) and (e) in Fig. 2] at 77.4°C. The glassy state stays till −65°C, the lowest temperature that could be achieved by the instrument. On subsequent heating from −65°C, the glassy phase transforms to the mesophase at 97.2°C, which remains unaltered till isotropic phase. It is

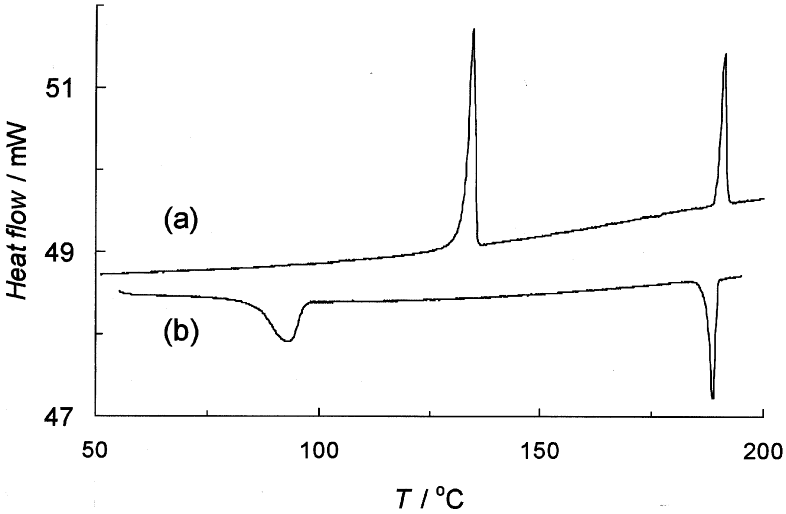


FIGURE 3 DSC traces obtained for the tetramer **1** at a rate of 5°C/min; (a) first heating scan from 50°C and (b) first cooling scan from isotropic phase.

known that upon keeping the sample at room temperature for a certain period of time, the glassy state slowly transforms into crystalline state. But this phenomenon does not seem to occur with the sample **2** even after several months. These transitions are also highly reproducible during repeated heating and cooling cycles. As a representative case the chemical stability of the sample **2** was investigated by taking DSC scans after keeping the sample at 110°C for 15 hours and found that the transition temperatures agree well with the previous runs.

X-RAY STUDIES

The diffraction patterns obtained in the mesophase of both the samples were quite similar. The pattern along with the derived one-dimensional intensity vs. 2θ profile obtained at 170°C with the tetramer **1** is shown in Figure 5 (a and b). In the low-angle region four sharp peaks are observed; one very strong and three weak reflections. Identifying the first peak with the Miller index (200), the four reflections confirm to the expected values from a two-dimensional rectangular lattice. In the wide-angle region there is a diffuse reflection corresponding to spacing of 4.7°A. Based on these features we propose that the mesophase could be a rectangular columnar ($\mathrm{Col_r}$) mesophase. This proposal is partially supported by the following

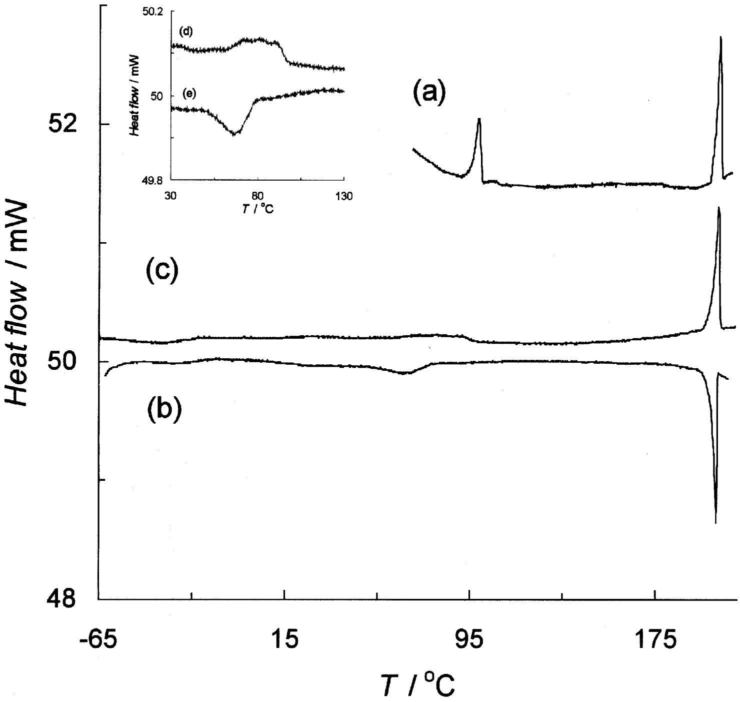


FIGURE 4 Differential scanning calorimeter traces obtained for tetramer **2** at a rate of 5°C/min.; (a) first heating, (b) subsequent cooling from isotropic liquid state to till −65°C and (c) subsequent heating from −65°C till the isotropic liquid transition. As can be seen neither crystallization nor melting peaks are observed instead peaks at 77.4°C and at 97.2°C corresponding to the transition between the glassy state and the mesophase appear during the cooling and the heating cycles (inset d and e) respectively.

observations. For some polar calamitic molecules [8c] and pure polycatenar compounds with non-polar chains no lamellar mesophase has been observed [10b]. This kind of a behavior especially in polycatenars is expected because of small differences in space filling between the rigid cores and the pendant terminal chains can be compensated by tilting of the aromatic cores with respect to the layer normal. If, however, the difference is substantial, tilting of molecule alone cannot sufficiently reduce this steric frustration. In such cases the layers may break up into ribbon-like aggregates which can organize to a columnar phase. Assuming such a structure, the lattice parameters are calculated to be a = 128°A and b = 37.2°A. However in the absence of a clear optical texture it is not possible to uniquely identify the mesophase. The appearance of a pseudoisotropic

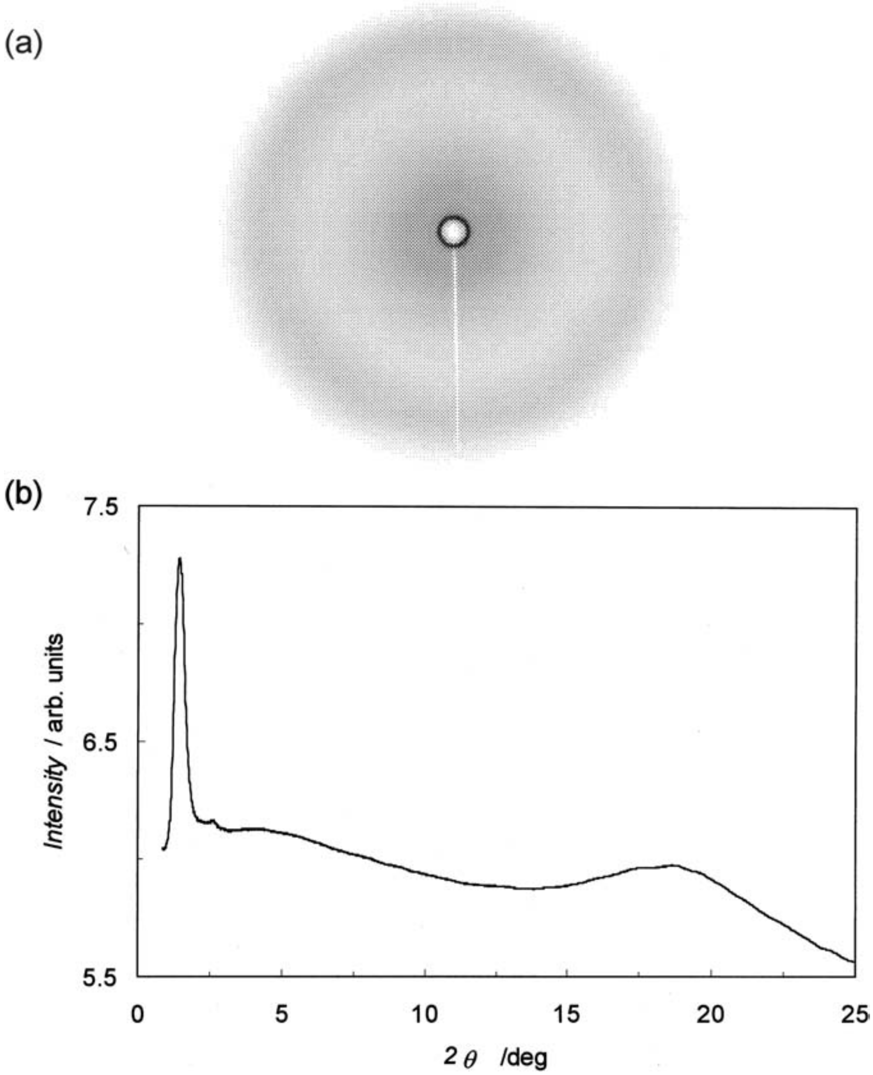


FIGURE 5 (a) X-ray diffraction pattern obtained at 170°C for the tetramer **1** (b) one-dimensional intensity vs. 2θ profile derived from the pattern shown in figure. Closely similar diffraction pattern has been observed for the tetramer **2**.

texture suggest that a uniaxial phase and hence the presence of a two-dimensional lattice seems to be contradictory. Detailed studies on this and related systems will shed more light on the possible structure.

SUMMARY

In conclusion we have achieved the synthesis of the first thermotropic monodispersive liquid crystalline tetramers possessing four non-identical anisometric entities connected by flexible spacers. Molecular design of these novel tetramers incorporates the cholesteryl ester (as a chiral entity), biphenyl (as a supportive entity for thermochromism), azobenzene (as photoactive mesogen), and tolan (as a half-disc) segments interconnected through even-even-odd (EEO) and odd-even-odd (OEO) paraffinic spacers. These compounds are thus multifunctional and such systems can possibly bridge the gap between rod-like and disc-like LCs. In addition, such OLCs can exhibit properties usually associated with polymers, whilst still retaining the fluidity and viscosity of low molar mass LCs and thereby bridging the gap between low molar mass LCs and high molar mass polymeric LCs. The concept of such molecular design originates from the novel approach that, by grafting different anisometric sub-units (mesogens) associated with a particular function/phenomenon in a single component system through covalent flexible linkages one can obtain supramolecular systems not only able to form thermotropic mesophases due to their anisotropic molecular shape but also capable of structure formation resulting from non-covalent intermolecular interactions. An exhaustive investigation focussing on molecular design and synthesis leading to multifunctional OLCs is very much essential in order to provide potential materials required for many practical applications.

EXPERIMENTAL

General Information

Chemicals were obtained from Fluka or Aldrich Company or a local source and used as such without any purification, while solvents were dried following standard procedures. Column chromatographic separation were performed using either silicagel or neutral aluminium oxide. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselge60.F254). IR spectra were recorded using Perkin Elmer Spectrum 1000 FT-IR spectrometer. ^{1}H NMR spetra were recorded using a Bruker DRX-500 (500 MHz) or Bruker AMX-400 (400 MHz) Bruker Aveance series DPX-200 (200 MHz) spectrometers. For ^{1}H NMR, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on Jeol JMS-600H spectrometer. The LC property of the tetramers were investigated using i) optical polarizing microscope (Leitz

DMRXP) in conjunction with a programmable hot stage (Mettler FP90) ii) differential scanning calorimeter (Perkin Elmer DSC7). Xray diffraction studies were carried out using an Image Plate Detector (MAC Science, Japan) equipped with a double mirror focussing optics and the sample contained in a Lindemann capillary tube.

General Procedure for the Preparation of Cholesteryl ω-[4′-(4-bromobutyloxy)biphenyl-4-oxy]alkanoates (3a and 3b):

A flask equipped with magnetic stir bar, reflux condenser and argon inlet was charged with **6a** or **6b** (2 g, 2.98 mmoles, 1eq) [19], anhydrous K_2CO_3 (1.7 g, 11.95 mmoles, 4eq), 1,4-Dibromobutane (4 g, 17.92 mmoles, 6eq) and dry acetone (15 ml). The reaction mixture was heated to 85°C for 24 hours. Evaporation of solvent afforded a white coloured mass which was extracted into CH_2Cl_2 (10 ml × 2). The organic layer was washed with brine and dried over Na_2SO_4. Upon evaporation of solvent a white solid was obtained which was purified by column chromatography using silica gel (100–200 mesh). Elution, first with Hexane followed by mixture of 5% EtOAc-Hexanes afforded the product as a pure white solid.

Cholesteryl 5-[4′-(4-bromobutyloxy)biphenyl-4-oxy] pentanoate (3a)

Yield = 85% (1.9 g); R_f value: 0.39 (10% Ethyl acetate-Hexanes); IR (KBr Pellet) υ_{max} in cm^{-1}: 2938, 2869, 1729, 1609, 1502, 1251, 1170; ^1H NMR (400 MHz, $CDCl_3$): 7.45 (d, $J = 8.56$ Hz, 4H, Ar), 6.93 (d, $J = 8.6$ Hz, 4H, Ar), 5.36 (brd, $J = 3.84$ Hz, 1H, Olefinic), 4.61 (m, 1H, CHOCO), 3.99 (m, 4H, 2 × OCH_2), 3.5 (t, $J = 6.58$ Hz, 2H, 1 × CH_2Br), 2.4-2.27 (m, 4H, 2 × allylic methylene), 2.12-1.05 (m, 34H, 14 × CH_2, 6 × CH), 1.01 (s, 3H, 1 × CH_3), 0.91(d, $J = 6.52$ Hz, 3H, 1 × CH_3), 0.87 (d, $J = 1.44$ Hz, 3H, 1 × CH_3), 0.85 (d, $J = 1.4$ Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3); FAB Mass: [M^+]: 787.6 Calcd for $C_{48}H_{69}O_4Br$.

Cholesteryl 6-[4′-(4-bromobutyloxy)biphenyl-4-oxy] hexanoate (3b)

Yield = 85% (1.9 g); R_f value: 0.39 (10% Ethyl acetate-Hexanes); IR (KBr Pellet): υ_{max} in cm^{-1}: 2939, 2867, 1736, 1607, 1501, 1250, 1170; ^1H NMR (400 MHz, $CDCl_3$): 7.45 (d, $J = 8.76$ Hz, 2H, Ar), 7.44 (d, $J = 8.76$ Hz, 2H, Ar), 6.92 (d, $J = 8.56$ Hz, 4H, Ar), 5.36 (brd, $J = 3.96$ Hz, 1H, Olefinic), 4.61(m, 1H, CHOCO), 3.99 (m, 4H, 2 × OCH_2), 3.5 (t, $J = 6.58$ Hz, 2H, 1 × CH_2Br), 2.36-2.28 (m, 4H, 2 × allylic methylene), 2.12-1.05 (m, 36H, 15 × CH_2, 6 × CH), 1.01(s, 3H, 1 × CH_3), 0.91(d, $J = 6.52$ Hz, 3H, 1 × CH_3), 0.87 (d, $J = 1.72$ Hz, 3H, 1 × CH_3), 0.85 (d, $J = 1.68$ Hz, 3H, 1 × CH_3), 0.67 (s, 3H, 1 × CH_3); FAB Mass: [M^+]: 801.6 Calcd for $C_{49}H_{71}O_4Br$.

1,2,3-Tridodecyloxybenzene (7)

A mixture of KOH (5.2 g, 92.6 mmoles, 6eq), dry DMSO (10 ml) was placed in a two necked round bottomed flask under continuous Argon flow and the reaction mixture was heated to 65°C. After the addition of Pyrogallol (2 g, 15.85 mmoles, 1eq) a brown colored solution was obtained. To this 1-Bromo dodecane (12.14 g, 48.72 mmoles, 3.2eq) was added dropwise and the reaction mixture was allowed to stir at the same temperature for 24 hours. Water was added to the cooled reaction mixture. The aqueous phase was repeatedly extracted into hexane (20 ml × 2). The combined organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvent gave a white solid which was purified with column chromatography on neutral Al_2O_3, elution with hexane afforded the product as a white solid. Yield = 84% (8.4 g); R_f value: 0.45 in Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 2915, 2849, 1597, 1502, 1256; ^1H NMR (400 MHz, $CDCl_3$): 6.90 (m, 1H, Ar), 6.53 (d, $J = 8.3$ Hz, 2H, Ar), 4.0(m, 6H, $3 \times OCH_2$), 2.0-1.0 (m, 60H, $30 \times CH_2$), 0.88 (t, $J = 6.4$ Hz, 9H, $3 \times CH_3$); Fab Mass: $[M^+]$: 630.5 Calcd for $C_{42}H_{78}O_3$.

2,3,4-Tridodecyloxyiodobenzene (8)

A mixture of compound (7) (2.87 g, 4.56 mmoles, 1eq), I_2 (578 mg, 2.27 mmoles, 0.5eq), Acetic acid (12.71 ml) was placed in round bottomed flask. After the addition of a few drops of con H_2SO_4 to the stirred reaction mixture a solution of HIO_3 (200 mg, 1.139 mmoles, 0.25eq) in water was added dropwise over period of 4–5 hours. After stirring the reaction mixture for 24 hours it was poured into 10% Na_2SO_3 solution and extracted with hexane (20 ml × 3). The combined organic phase was washed with a saturated solution of Na_2CO_3 and then washed with brine and dried over Na_2SO_4. Evaporation of the solvent yielded a white solid which was purified by column chromatography using 230–400 mesh silica gel, upon elution with hexane pure product was obtained as white solid. Yield: 2.0 g (58%); R_f value: 0.21 in Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 2922, 2853, 1463, 1087; ^1H NMR (400 MHz, $CDCl_3$): 7.37 (d, $J = 8.7$ Hz, 1H, Ar), 6.5 (d, $J = 9$ Hz, 1H, Ar), 4.0 (m, 6H, $3 \times OCH_2$), 1.45-1.1 (m, 60 H, $30 \times CH_2$), 0.88 (t, $J = 6.6$ Hz, 9H, $3 \times CH_3$); Fab Mass: $[M^+]$: 756.0 Calcd for $C_{42}H_{77}O_3I$.

4-[2,3,4-tridodecyloxyphenyl]-2-methyl-3-butyn-2-ol (9)

A mixture of compound (8) (1 g, 1.332 mmoles, 1eq), 2-methyl-3-butyn-2-ol (0.2 g, 2.2 mmoles, 1.5eq), bis (triphenylphosphine)palladium(II) chloride (8 mg, 0.01 mmole, 0.5%), triphenylphosphine (14.8 mg, 0.056 mmole, 2.5%) and copper(I)iodide (8.6 mg, 0.045 mmoles, 2%) in dry triethylamine(5 ml) was stirred at 65°C under Argon atmosphere for 16 hours. The reaction mixture was cooled and filtered through celite bed. The filtrate was evaporated *in vacuo* to get a pale yellow oil which was then purified by column chromatography using silica gel (100–200 mesh). Elution with mixture of 10% EtOAc-Hexane furnished a pale yellow coloured viscous mass. Yield: 0.8 g (85%); R_f value: 0.25 in 30% CH_2Cl_2-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 3368, 2931, 2878, 1203; ^1H NMR (400 MHz, $CDCl_3$): 7.04 (d, $J = 8.7$ Hz, 1H, Ar), 6.5 (d, $J = 8.4$ Hz, 1H, Ar), 4.0 (m, 6H, 3 × OCH_2), 1.45-1.1 (m, 61H, 30 × CH_2, 1 × OH), 1.61(s, 6H, 1 × CH_3), 0.88 (t, $J = 6.75$ Hz, 9H, 3 × CH_3); Fab Mass: [M^+]: 711.7 Calcd for $C_{47}H_{84}O_4$.

2,3,4-Tridodecyloxyphenylacetylene (10)

A mixture of Compound (9) (1 g, 1.404 mmoles, 1eq), KOH (400 mg, 7.02 mmoles, 5eq) and dry toluene (10 ml) was heated to reflux for 2 hours under Argon atmosphere. The solvent was evaporated to dryness *in vacuo* and the brown semisolid obtained was poured into ice-cold water (50 ml). The aqueous layer was extracted into hexanes (20 ml × 2). The organic layer was then washed with brine and dried over Na_2SO_4. Evaporation of solvent furnished pale brown oil which was further purified by column chromatography using alumina (neutral). Hexanes elution furnished a pale yellow viscous liquid. Yield: 0.65 g (65%); R_f value: 0.53 in 10% EtOAc-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 2924, 2854, 2106, 1592; ^1H NMR (400 MHz, $CDCl_3$): 7.11 (d, $J = 8.6$ Hz, 1H, Ar), 6.56 (d, $J = 8.6$ Hz, 1H, Ar), 4.1 (m, 6H, 3 × OCH_2), 3.13(s, 1H, alkyne H), 1.9-1.1 (m, 60H, 30 × CH_2), 0.88 (t, $J = 6.47$ Hz, 9H, 3 × CH_3); Mass: [M^+]: 654.8 Calcd for $C_{44}H_{78}O_3$.

4-[(2,3,4-Tridodecyloxy)phenylethynyl]-O-(tetrahydro pyran-2-yl)phenol (11)

A mixture of compound (10) (1 g, 1.52 mmoles, 1.1eq), 4-Iodo-O-(tetrahydro-pyran-2-yl)phenol (0.424 g, 1.53 mmoles, 1.01eq), bis(triphenyl phosphine)palladium(II) chloride (8 mg, 0.01 mmole, 0.5%), triphenylphosphine (14.8 mg, 0.056 mmoles, 2.5%) and copper(I)iodide (8.6 mg, 0.045 mmoles, 2%) in dry Triethylamine(5 ml) and dry THF (5 ml) was stirred at 65°C under Argon atmosphere for 16 hours. The reaction mixture was cooled and filtered through celite bed. The filtrate was evaporated *in vacuo* to get pale yellow oil which was then purified by column chromatography using silica gel (100–200 mesh) . Elution with a mixture of 10% EtOAc-Hexane furnished a pale yellow coloured viscous mass. Yield: 0.77 (78%); R_f value: 0.4 in 30% CH_2Cl_2-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 2923, 1510, 1239, 1094; ^1H NMR (400 MHz, $CDCl_3$) : 7.42 (d, $J = 8.8$ Hz, 1H, Ar), 7.12 (d, $J = 8.6$ Hz, 2H, Ar), 7.0 (d, $J = 8.8$ Hz, 1H, Ar), 6.59 (d, $J = 8.6$ Hz, 2H, Ar), 5.42 (t, $J = 3.12$ Hz, 1H, 1 × CHOCO), 4.0 (m, 8H, 4 × OCH_2), 2.1-1.18 (m, 66H, 33 × CH_2), 0.87 (t, $J = 6.44$ Hz, 9H, 3 × CH_3); Mass: [M^+]: 745.61 Calcd for $C_{55}H_{90}O_5$.

4-[(2,3,4-Tridodecyloxy)phenylethynyl]phenol (12)

Compound 11(1 g, 1.2 mmoles) was taken in a mixture of THF and MeOH and a pinch of PTSA was added and stirred for 30 minutes. Solvent was removed under *vacuo* to get a brown coloured mass, which was diluted with CH_2Cl_2 and washed with $NaHCO_3$ followed by brine and dried over Na_2SO_4. Evaporation of solvent furnished a brown colored mass which was purified by column chromatography using 60–120 mesh silica gel. Elution with 20% EtOAc-Hexanes furnished a pale yellow viscous mass. Yield: 0.68 (78%); R_f value: 0.2 in 10% EtOAc-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 3381, 2923, 2853, 1608, 1270; ^1H NMR (400 MHz, $CDCl_3$): 7.39 (d, $J = 8.56$ Hz, 2H, Ar), 7.12 (d, $J = 8.6$ Hz, 1H, Ar), 6.78 (d, $J = 8.56$ Hz, 2H, Ar), 6.59 (d, $J = 8.6$ Hz, 1H, Ar), 5.06 (brs, 1H, 1 × OH), 4.0 (m, 6H, $3 \times OCH_2$), 1.9-1.0 (m, 60H, $30 \times CH_2$), 0.88 (t, $J = 6.74$ Hz, 9H, $3 \times CH_3$); Mass: [M^+]: 745.9 Calcd for $C_{50}H_{82}O_4$.

4-[(2,3,4-Tridodecyloxy)phenylethynyl]-(5-bromopentyl oxy)benzene (13)

A 100 ml flask equipped with water condenser and argon inlet, was charged with acetone (HPLC grade, 50 ml), anhydrous potassium carbonate (1.47 g, 10.68 mmoles, 4eq), compound 12 (2 g, 2.67 mmoles, 1eq), and 1,5-Dibromopentane (3.68 g, 16.02 mmoles, 6eq), and then flushed with argon for some time. After closing the neck with a septum, the reaction mixture was heated to reflux for 24 hours with vigorous stirring and filtered hot through a celite bed. The filtrate was evaporated and the crude mass obtained was dissolved in CH_2Cl_2, washed with brine, dried over Na_2SO_4. Evaporation of solvent gave an off white solid which was purified by column chromatography using silica gel(100–200 mesh). Elution with a mixture of 5% EtOAc-Hexanes yielded a white solid. Yield: 0.68 (78%); R_f value: 0.4 in 30% CH_2Cl_2-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 2923, 2853, 1606, 1286; ^1H NMR (400 MHz, $CDCl_3$): 7.42 (d, $J = 9$ Hz, 2H, Ar), 7.14 (d, $J = 8.5$ Hz, 1H, Ar), 6.83 (d, $J = 9$ Hz, 2H, Ar), 6.59 (d, $J = 8.5$ Hz, 1H, Ar), 4.0 (m, 6H, $2 \times OCH_2$), 3.44 (t,$J = 7$ Hz, 2H, CH_2Br), 1.9-1.0 (m, 66H, $33 \times CH_{2,}$), 0.88 (t, $J = 6.6$ Hz, 9H, $3 \times CH_3$); Mass: [M^+]: 894.8 Calcd for $C_{55}H_{91}O_4Br$.

4-Hydroxy-4′-methoxyazobenzene (14)

$NaNO_2$ (6.9 g, 100 mmoles, 1eq) was added dropwise to a well stirred and precooled solution of p-Anisidene (12.3 g, 100 mmoles, 1eq) in mixture of 40 ml H_2O and 30 ml Conc H_2SO_4. The resulting diazonium solution was quenched with a solution of Phenol (9.4 g, 100 mmoles, 1eq) in NaOH(4 g) and Na_2CO_3 (12 g) in 100 ml of water at 0–5°C. As the reaction mixture was allowed to warm up to room temperature an orange coloured solid precipitates out which was filtered on a buchner funnel. The air dried sample was further purified by repeated recrystallization from aqueous EtOH. Yield: quantitative; R_f value: 0.4 in 30% EtOAc-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 3332, 1597, 1239; ^1H NMR (200 MHz, $CDCl_3$): 7.85 (m, 4H, Ar), 6.9 (m, 4H, Ar), 3.88 (s, 3H, 1 × OCH_3), 1.6 (brs, 1H, 1 × OH); FAB Mass: [M^+]: 227.92 Calcd for $C_{13}H_{12}O_2N_2$.

1-(4-Hydroxyazobenzene-4-oxy)-5-{[(2,3,4-tridodecyloxy)-phenylethynyl]phenoxy}-pentane (4)

A mixture of 13 (1 g, 1.09 mmoles, 0.5eq), 4,4′-dihydroxyazobenzene (560 mg, 2.61 mmoles, 1.2eq), anhydrous K_2CO_3 (0.6 g, 4.4 mmoles, 2eq) in Dry DMF was heated at 70°C for 24 hours under Argon atmosphere. The cooled reaction mixture was poured into water and the aqueous layer was extracted into CH_2Cl_2 (2 × 20 ml). The combined organic layer was washed with brine dried over Na_2SO_4. Evaporation of the solvent gave an orange coloured solid which was purified by column chromatography using 100–200 mesh silica gel. Upon elution with 10% EtOAc-Hexanes, orange coloured crystals were obtained. Yield: 0.4 g (40%); R_f value: 0.25 in 30% EtOAc-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 3304, 2919, 2851, 1603, 1510; ^1H NMR (400 MHz, $CDCl_3$): 7.85 (d, $J = 8.84$ Hz, 2H, Ar), 7.82 (d, $J = 8.76$ Hz, 2H, Ar), 7.42 (d, $J = 8.48$ Hz, 2H, Ar), 7.12 (d, $J = 8.56$ Hz, 1H, Ar), 6.98 (d, $J = 8.76$ Hz, 2H, Ar), 6.92 (d, $J = 8.64$ Hz, 2H, Ar), 6.85 (d, $J = 8.52$ Hz, 2H, Ar), 6.59 (d, $J = 8.64$ Hz, 1H, Ar), 5.20 (brs, 1H, -OH), 4.12 (m, 10H, 5 × OCH_2), 1.97-1.15 (m, 66H, 33 × $CH_{2,}$), 0.87 (t, $J = 6.68$ Hz, 9H, 3 × CH_3); Mass: [M^+]: 1028.00 Calcd for $C_{67}H_{100}O_8N_2$.

4,4′- Dihydroxyazobenzene (15)

$AlCl_3$ (Excess, 4 g) was added to well stirred solution of Compound (14) (0.91 g, 4 mmoles, 1eq) in $CHCl_3$ placed in a 2 necked round bottomed flask equipped with a water condenser and N_2 inlet, and was heated to 50°C. Dry Pyridine (8.4 ml) was added dropwise through the second neck over a period of 1 hour. The reaction mixture was then refluxed for 30 hours and then cooled to 0°C and acidified with 10% HCl. The product was extracted into diethyl ether (20 ml × 3). The combined ether layer was repeatedly washed with cold water. Upon evaporation of the solvent an orange coloured solid was obtained which was purified by column chromatography on silica gel (100–200 mesh). Upon elution with 20% EtOAc-Hexanes initially the unreacted starting material elutes and then with 30% EtOAc-Hexanes the pure product elutes out. Yield: 40% (1.8 g); R_f value: 0.21 in 30% EtOAc-Hexanes; IR (KBr Pellet) υ_{max} in cm^{-1}: 3326, 1583, 1213; ^1H NMR (200 MHz, $CDCl_3$): 7.87 (m, 4H, Ar), 6.9 (m, 4H, Ar); FAB Mass: [M^+]: 214 Calcd for $C_{12}H_{10}O_2N_2$.

Tetramer 1 and 2

A mixture of compound **3a** or **3b** (0.4 g, 0.5 mmoles, 1eq), compound 4 (0.56 g, 5.54 mmoles, 1.1eq), and anhydrous K_2CO_3 (1.1 g, 2.5 mmoles, 5eq) was heated at 85°C for 24 hours under Argon atmosphere. The cooled reaction mixture was poured into water and the aqueous layer was extracted into CH_2Cl_2 (2×20 ml). The combined organic layer was washed with brine dried over Na_2SO_4. Evaporation of the solvent gave an orange coloured solid which was purified by column chromatography using 100–200 mesh silica gel. Upon elution with 10% EtOAc-Hexanes, orange coloured crystals were obtained. **1**: $R_f = 0.57$ (**4**:**1** CH_2Cl_2-Hexanes). A yellow solid; m.p. 202°C; Yield: 177 mg (42%); IR (KBr pellet): γ_{max} 2923, 2852, 1730, 1603, 1581 and 1513 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 7.87 (d, $J = 8.88$ Hz, 4H, Ar), 7.46 (m, 6H, Ar), 7.13 (d, $J = 8.6$, 1H, Ar), 7.01 (d, $J = 2.76$, 2H, Ar), 6.98 (d, $J = 2.76$, 2H, Ar), 6.95 (d, $J = 7.32$, 2H, Ar), 6.93 (d, $J = 7.36$, 2H, Ar), 6.85 (d, $J = 8.88$, 2H, Ar), 6.60 (d, $J = 8.76$, 1H, Ar), 5.37 (brd, $J = 4.52$, 1H, Olefinic), 4.62 (m, 1H, -CH-O-CO-), 4.02 (m, 16H, $8 \times$ -OCH_2-), 2.32 (brt, $J = 7.38$, 4H, $2 \times$ allylic methylene), 2.03-0.86 (m, 117H, $5 \times$ -CH_3, $48 \times$ -CH_2-, $6 \times$ -CH-), 1.01 (s, 3H, -CH_3), 0.86 (d, $J = 4.8$, 3H, -CH_3) and 0.68 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, Spin Echo FT): 172.77 (CO), 161.12 (C), 161.01 (C), 158.82 (C), 158.06 (C), 154.36 (C), 153.99 (C), 147.07 (C), 141.98 (C), 139.7 (C), 133.56 (C), 132.78 (CH), 127.67 (CH), 127.47 (CH), 124.33 (CH), 122.53 (CH), 116.05 (C), 114.78 (CH), 114.68 (CH), 114.46 (CH), 111.03 (C), 108.20 (CH), 91.59 (C), 84.7 (C), 74.22 (CH_2), 73.82 (CH), 73.76 (CH_2), 68.84 (CH_2), 68.05 (CH_2), 67.77 (CH_2), 67.54 (CH_2), 56.71 (CH), 56.18 (CH), 50.01 (CH), 42.33 (CH_2), 39.76 (CH_2), 39.53 (CH_2), 38.12 (CH_2), 37.01 (CH_2), 36.61 (CH_2), 36.21 (CH_2), 35.79 (CH), 34.59 (CH_2), 31.92 (CH_2), 30.52 (CH_2), 30.34 (CH_2), 29.69 (CH_2), 29.36 (CH_2), 29.00 (CH_2), 28.22 (CH_2), 28.00 (CH), 27.84 (CH_2), 26.25 (CH_2), 26.12 (CH_2), 26.04 (CH_2), 25.64 (CH_2), 24.81 (CH_2), 24.28 (CH_2), 23.85 (CH_2), 22.79 (CH_3), 22.68 (CH_2), 22.55 (CH_3), 21.04 (CH_2), 19.23 (CH_3), 18.72 (CH_3), 14.08 (CH_3) and 11.86 (CH_3); FAB Mass: 1737.0 [MH]+; Elemental analysis calcd. for $C_{116}H_{168}N_2O_{10}$: C 79.5, H 9.78 and N 1.59; found C 79.25, H 9.86 and N 1.21.

Tetramer **2**: For molecular structural characterization data refer to our publication [21].

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