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Synthesis and thermal properties of liquid crystal trimers comprising cyanobiphenyl and salicylaldimine anisometric segments

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ABSTRACT

The synthesis and mesomorphism of a series of liquid crystal trimers made by covalently linking two cyanobiphenyl moieties with a central salicylaldimine core through two flexible spacers are reported. Nine different oxyalkyleneoxy spacers varying in the number of carbon atoms and thus, methylene units from 3 to 11 were used to understand structure–mesomorphic property correlations. The optical microscope and differential scanning calorimeter were employed to evaluate their phase transitional behavior. All the trimers exhibit an enantiotropic uniaxial nematic phase over a wide thermal range (>80 °C) while a homolog comprising an octamethylene (even-parity) spacer displays, additionally, a metastable smectic phase. The nematic-isotropic transition temperatures critically depend on the parity of the spacer with the values for the odd-parity spacer containing homologs being lower than those of the even members, a feature generally observed in oligomesogens.

1. Introduction

The field involving the design and synthesis of thermotropic liquid crystals (LCs) has emerged as an area of active research since such materials are attractive from both fundamental research and practical application view points.[1–3] This is especially noteworthy in case of conventional LCs such as rod-like (calamitic) and disc-like (discotic) mesogens[2] as well as polymeric LCs[3] to some extent. However, in recent years the studies are also focused on the molecular engineering and synthesis of the intermediate molecular architectures called supermolecular LCs (oligomesogens) wherein several mesogenic segments are covalently combined through flexible spacers.[1,4–23] This is because oligomesogens offer a practical means of introducing desirable and different functionalities through the combination of appropriate functional mesogenic segments. In fact, they can be made to exhibit properties usually associated with polymers while still retaining the fluidity and viscosity of low molecular weight LCs. Moreover, they display interesting thermal properties owing to their nonconventional anisotropic molecular shape and their complex noncovalent intermolecular interactions. Of the several kinds of LC oligomers reported hitherto, the linear supermolecules composed of two to several classical rod-like or disk-shaped segments bound linearly via flexible spacer(s) have been the focus of considerable research interest not only for their remarkable liquid crystal behavior but also since they serve as model compounds for semi-flexible main chain LC polymers. Hitherto, dimers, trimers, tetramers, and pentamers, respectively, made up of two, three, four, and five mesogenic segments interlinked via one, two, three, and four spacers, respectively, have been prepared and their thermal behavior is evaluated. However, in the context of the present work we restrict our discussion to linear liquid crystal trimers consisting of calamitic segments only.

Liquid crystalline linear trimers (also referred to as trimesogens or triplet LCs),[7,11–27] wherein three rod-like mesogenic entities are tide terminally through two flexible spacers, are considered as an important class of oligomers not only because of their interesting thermal behavior but also they help in studying how the LC behavior evolves from dimers to polymers.[7] Thus far, three obvious kinds of trimers viz., symmetric[13,18,23]—where all the constituent mesogenic (A–A–A) units are identical, mixed[11,12,14–17,21,22,24–27]—two of the mesogens (A–B–A) are identical, and nonsymmetric[19,20]—none of the mesogenic (A–B–C) units are identical, have been prepared and characterized. Seemingly, the mixed trimers, including supramolecular[28,29] systems (where the mesogenic segments are formed/linked through the hydrogen-bond interactions) and metal-containing ones,[21] are reported in large numbers. The thermal behavior of such trimers is known to be generally dependent on the parity of the spacers as well as the molecular structures of the terminal and central mesogenic cores; these features are similar to those observed for both dimers and LC main chain polymers. For example, the clearing temperatures and the associated entropy change exhibit an odd–even effect as the parity of the spacer is varied. Particularly, the trimers with even-parity spacers exhibit higher values

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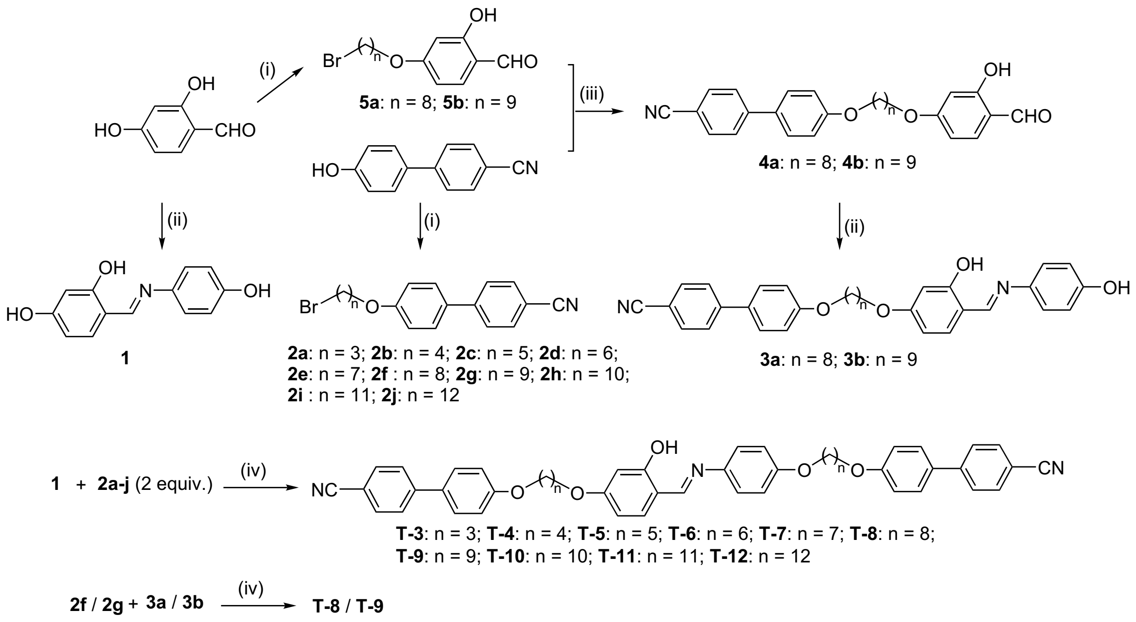
when compared to odd-parity spacer containing members. Most importantly, the electronic nature of the mesogenic (aromatic) segments is proven to be important in the context of inducing functional properties and stabilization of mesophases, especially the smectic phase. Kelly et al., have recently reported the photoluminescent and electroluminescent LC trimers formed by covalently linking an aromatic light emitting central core with two cholestanyl entities through two flexible spacers.[27]

The trimers consisting of electron deficient (cyanobiphenyl) unit(s), and electron rich (Schiff's base/azobenzene) core(s) exhibit nematic and/or smectic behavior.[14,24–26] In particular, trimers (**TAZO*n*** series) formed by tethering two cyanobiphenyls with a central electron rich azobenzene core through two flexible spacers of varying length and parity display smectic behavior solely.[14] In fact, Imrie and Luckhurst showed that if the central azobenzene unit is replaced by a relatively less electron rich biphenyl core the resultant symmetric trimers (**TCBO*n*** series) exhibit enantiotropic nematic (N) and metastable smectic A (SmA) phases.[18] The favored smectic behavior of the trimers of **TAZO*n*** series must be evolving as a result of the specific interaction between the dissimilar azobenzene and cyanobiphenyl mesogenic cores. In other words, this behavior can be assumed to be originating, as in the case of nonsymmetric dimers,[30] from the electrostatic quadrupolar interactions between the dissimilar mesogens with quadrupole moments of opposite sign. However, recently we observed that the mixed trimers (**TM-*n*** series) made by joining a bent-shaped core, derived from more electron rich salicylaldimine units, and electron deficient cyanobiphenyls entities through two alkylene spacers of varying length and parity exhibit an enantiotropic nematic behavior.[26] Seemingly, this behavior is contrary to the expectation that these trimers with more electron rich segments, as in the case of **TAZO*n*** series, should have exhibited smectic behavior. These results suggest that the **TM-*n*** series trimers are more compatible with the molecular assembly in the nematic structure than the layered structure. In order to find out whether the presence of bent-core segment at the center of these trimers is the cause for their self-assembly into nematic structure, we prepared a homologous series of trimers where the cyanobiphenyl moieties are covalently tethered to both the ends of rod-like salicylaldimine [*N*-(2-hydroxy-4-alkoxy-benzylidene)aniline] segment through oxyalkyleneoxy spacer of varying length and parity. Besides, the motivation for this particular design stemmed from our observation that combination of cyanobiphenyl and salicylaldimine moieties lead to the molecular systems capable of exhibiting biaxial mesophases.[31,32] Here we present the synthesis and LC behavior of a series of mixed trimers namely, 4′-(ω-(4-(4-(ω-(4′-cyanobiphenyl-4-yloxy)alkoxy)-2-hydroxybenzylideneamino)-phenoxy)-alkoxy)biphenyl-4-carbonitrile. The general molecular structure of these new trimers is shown in Scheme 1 and we hereafter refer to them as **T-*n*** series of trimers where **T** stands for trimer and ***n*** signifies the number of methylene units in the flexible alkylene spacers.

2. Synthesis and characterization

Owing to the purity and yield problems associated with the target LC trimers, which originated as a result of their poor solubility in common organic solvents,[18] two synthetic pathways were employed (see Scheme 1). Initially, it was envisaged that the target oligomers can be prepared by the condensation of hydroxy compounds (**3a**/**3b**) with bromoalkanes (**2f**/**2g**). The suitability of this contemplation with regard to above-mentioned difficulties was tested by preparing some representative trimers viz., **T-8** and **T-9**. The hydroxy compounds (**3a** and **3b**) were synthesized in three steps starting from 2,4-dihydroxybenzaldehyde. It was first subjected to selective mono-O-alkylation with 1,8-dibromooctane and 1,9-dibromononane in the presence of K_2CO_3 as a mild base in refluxing butanone to obtain compounds **5a** and **5b**, respectively. The reaction of these materials (**5a** and **5b**) with readily available 4′-hydroxybiphenyl-4-carbonitrile in the presence of a mild base yielded salicylaldehydes **4a** and **4b**, which on condensing with 4-aminophenol furnished the precursors **3a** and **3b**. The other known precursors **2f** and **2g**, including **2a**–**e** and **2h**–**j**, were prepared by alkylating 4′-hydroxybiphenyl-4-carbonitrile with appropriate α,ω-dibromoalkanes.[32,33] The selective mono-O-alkylation of **3a** and **3b** with bromoalkanes **2f** and **2g** yielded trimers **T-8** and **T-9**, respectively. However, these trimers were found to be contaminated with the starting hydroxy compounds (**3a** and **3b**). Indeed, they were purified by repeated recrystallization during which their quantity was lost considerably. Therefore, in an alternative route



Scheme 1. Reagents and condition: (i) dibromoalkanes, anhyd K_2CO_3, butanone, reflux, 48 h; (ii) 4-aminophenol, ethanol, AcOH (catalytic), reflux 2 h; (ii) anhyd K_2CO_3, KI (catalytic) butanone, reflux, 48 h; (iv) anhyd K_2CO_3, butanone, reflux, 48 h.

Table 1
Phase transitions temperatures[a] (°C) and the corresponding enthalpies (J/g) of liquid crystalline trimers (**T-*n*** series) and intermediates **3a** and **3b**

Compound	*n*	Cr	Heating cooling	SmX	Heating cooling	N	Heating cooling	I
T-3	3	●	191.5[20.9][b] 100[18.8]	—	—	●	224.6[1.7] 222.1[1.6]	●
T-4	4	●	194.9 [20.1]			●	308[c]	—
T-5	5	●	174.4[49.9] 115.9[27.2]	—	—	●	219.4[1.4] 217.0[1.3]	●
T-6	6	●	179.1[24.9] 131.5[9.8]	—	—	●	264.6[3] 262.7[2.9]	●
T-7	7	●	152.2[46.8] 106.3[43.5]	—	—	●	216.6[1.8] 214.5[1.8]	●
T-8	8	●	166.8[49.6] 114.2[31.5]	●	— 122.4 [2]	●	243.1[3.2] 242.1[3.1]	●
T-9	9	●	152.9[88.3] 105.9[66.5]	—	—	●	207.1[2.1] 205.3[2]	●
T-10	10	●	173.6[14.9][b] 138.9[16.7]	—	—	●	197.2[2.6] 194.8[2.5]	●
T-11	11	●	132.6[21.6][b] 97.5[30.4]	—	—	●	189.5[2.3] 187.7[2.2]	●
T-12	12	●	148.2[51.3] 116.8[45.2]	—	—	●	189.4[2.3] 188.0[2.2]	●
3a	8	●	199.7[65.0] 157.3[47.9]	—	—	●	206.3[4.4] 203.2[4.3]	●
3b	9	●	174.5[67.4] 141.4[58.7]	—	—	●	181.6[4.4] 179.3[4.3]	●

[a] Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C/min.
[b] Compounds **T-3**, **T-10** and **T-11** show additional Cr to Cr transitions during the first heating cycle at 182 °C [48.9], 191.5 [20.8], and 108.5 [25.4], respectively.
[c] The sample decomposes at this temperature. I=isotropic liquid state; N=nematic phase, Cr=crystal and SmX=unknown smectic phase.

a trihydroxy compound **1**, namely 4-((4-hydroxyphenylimino)methyl)-benzene-1,3-diol, was subjected to selective di-O-alkylation with 2 equiv of bromoalkanes **2a–j** in the presence of K_2CO_3 and 2-butanone at reflux to obtain the desired trimers with high purity and good yields. Compound **1** was prepared by acid catalyzed condensation of 2,4-dihydroxybenzaldehyde with 4-aminophenol. All new compounds were satisfactorily characterized by spectroscopic methods and elemental analysis (see Section 4 for synthetic procedures and characterization data).

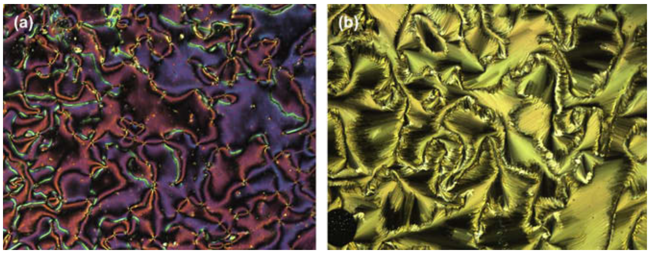


Figure 1. Optical microphotographs obtained for (a) the nematic schlieren texture of trimer **T-7** at 210 °C and (b) the paramorphotic schlieren texture of the SmX phase occurring below the nematic phase of trimer **T-8** (at 122 °C).

3. Results and discussions

3.1. Mesomorphic behavior

The identification of the phases and determination phase transition temperatures were achieved with the help of polarizing optical microscope (POM). The sample placed between a clean untreated glass slide and a cover slip was used for this particular study. The mesophase assignment was based on the observation of birefringence and fluidity when examined under POM. To confirm the transition temperatures and to determine their associated enthalpies, a differential scanning calorimeter (DSC), calibrated using pure Indium, was employed. The peaks observed in DSC traces (obtained at a rate of 5 °C/min) due to phase transitions were reproducible and peak temperatures were consistent with those deduced from the optical experiments. The results of these combined studies are presented in Table 1. It is clear from Table 1 that all the trimers exhibit enantiotropic mesomorphism, especially the nematic (N) behavior. Notably, the trimer **T-8** with an octamethylene spacer displays another mesophase, which is metastable, albeit. It may be mentioned here that the intermediates **3a** and **3b** also stabilize nematic phase (see Table 1).

The nematic behavior occurring in each member was established based on the observation of following textural features under POM. On cooling the isotropic liquid of any homolog placed between a pair of clean glass slides, nematic phase appears with droplets emanating from the dark background. Within the droplets curved dark brushes (schlieren pattern) with director fluctuations occur. On cooling further, the nematic droplets coalesce to give classical schlieren texture of high birefringence with both two-brush (defect strength $s=\pm1/2$) and four-brush ($s=\pm1$) defects; as a representative case such a pattern observed at 210 °C for the **T-7** member is shown in Figure 1a. On further cooling, the schlieren texture transforms to a threaded pattern, and in some regions marble texture was also noted. The texture flashed when subjected to mechanical stress. The usage of substrates treated for either planar or homeotropic alignments seemed to have no much effect on the textural patterns. For all the homologs, except **T-8**, cooling the nematic phase results in crystallization of the sample. The **T-8** member stabilizes a monotropic mesophase below the nematic phase. This phase exhibits a focal-conic pattern along with the paramorphotic schlieren texture (of the nematic phase), as shown in Figure 1b, which points to the smectic structure and thus, is labeled as SmX phase. The DSC trace in the cooling cycle indeed provides the signature for the N-SmX phase transition (Fig. 2). Owing to metastable nature of the SmX phase, the detailed structural characterization by X-ray diffraction study was not possible.

It is well documented that the thermal behavior of linear LC trimers largely depends on the number of carbon atoms in the two identical flexible spacers.[7,11–27] Specifically, the transition temperatures display a remarkable odd-even effect as the length and parity of the spacer are varied. Such a feature is also seen in the present **T-*n*** series of trimers, as expected. Figure 3 depicts the dependence of the transition temperatures on the spacer-length, the number of methylene units (*n*) in the aliphatic flexible spacer. It can be seen from the figure that the crystal-nematic (melting) and nematic-

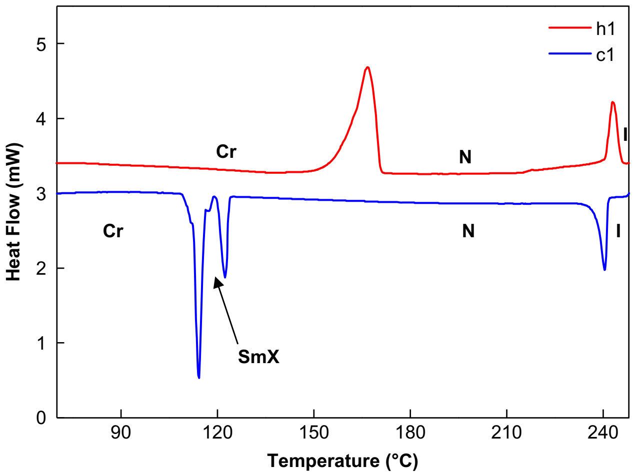


Figure 2. The DSC traces obtained for compound **T-8** during the first heating (h1) and cooling (c1) cycles at a rate of 5 °C/min.

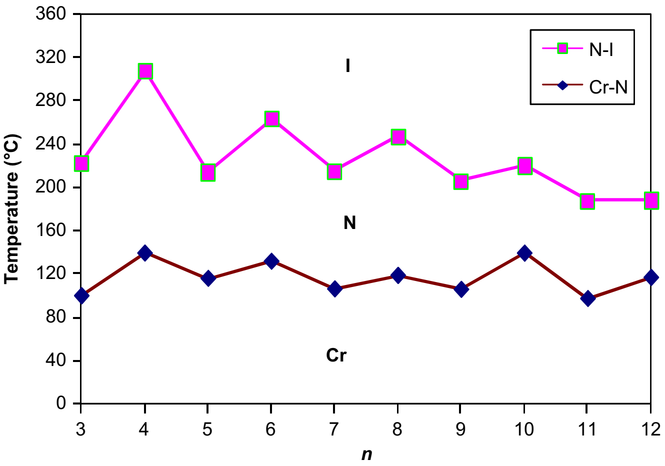


Figure 3. Phase diagram of temperature vs number of methylene units in the spacers for **T-*n*** series.

isotropic temperatures show odd-even effect; especially, the latter exhibits a pronounced odd-even effect, wherein the trimers with even-parity spacer possess the higher values. Furthermore, unlike the melting temperatures, the nematic-isotropic temperatures attenuate upon increasing the number of methylene (***n***) units, which is analogous that observed for other LC trimers.[7] The observed odd-even effect in the clearing point temperatures with respect to variation in the number of methylene units has been convincingly interpreted in terms of the overall molecular shape of the trimers directed from the geometry and flexibility of the spacers.[7] The molecular structure of an odd-membered trimer, for example, **T-5** with a pentamethylene spacer, in its most extended all-trans conformation (energy minimized) deduced from MM2 computations of CS Chem Draw 3D (version 5) program, appear like a well stretched 'S' (Fig. 4a) where the central salicylaldimine core and the two terminal cyanobiphenyl cores are inclined with respect to each other; thus, it possesses a reduced shape-anisotropy that accounts for the lower clearing temperature. Whereas, in the energy minimized molecular structure of a trimer with an even-parity spacer, for example, compound **T-6** with an hexamethylene spacer, all the mesogenic segments lie almost along an axis and thus, bears a resemblance to an extended rod. Such a molecular shape enables the even members to pack more closely resulting in higher transition temperatures.

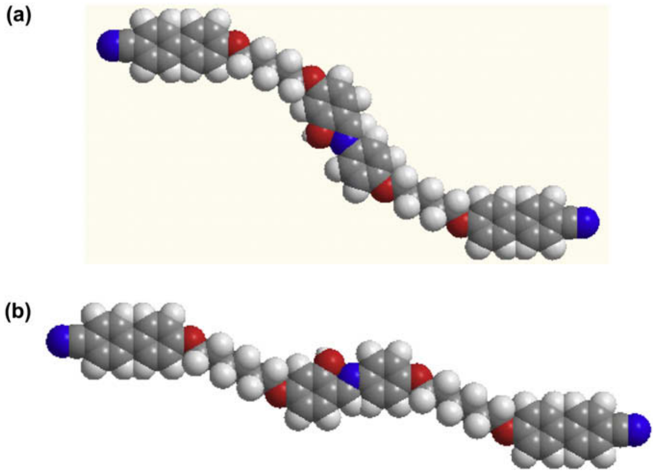


Figure 4. Energy minimized (all-trans conformation) space filling models of the molecular structures of trimers (a) **T-5** and (b) **T-6**.

3.2. Summary

The first examples of salicylaldimine-based liquid crystalline trimers have been synthesized and investigated for their phase behavior. Particularly, they are formed by covalently tethering nematogenic cyanobiphenyl segments on the either side of salicylaldimine core through flexible spacers. The molecular design was chosen to understand structure–property correlations, and in fact, was originated based on our general observation that the molecular systems consisting of cyanobiphenyl and salicylaldimine favor the stabilization of biaxial mesophase(s). All the homologs, exhibit only the uniaxial nematic phase with the exception of an octamethylene-spacer containing member, which stabilizes an additional monotropic smectic phase. This implies therefore that these trimers are more compatible with the molecular assembly in the nematic structure than the layered structure. It can also be seen that this trimeric design, although consisting of favorable mesogenic segments, do not support the stabilization of biaxial mesophase. The effects of odd-parity and even-parity spacers on the transition temperatures, especially the clearing temperatures, are quite apparent; the even members possess higher value, in a manner reminiscent of other reports. The present investigation may be useful for the better understanding of the relation between chemical structure and physical properties of such mixed trimers.

4. Experimental

4.1. General information

The chemicals procured were used without any further purification. 2-Butanone and ethanol obtained were purified and dried as per the standard procedures. The target trimers were purified by recrystallization choosing appropriate mixture of solvents; while the intermediates, depending upon the need, were purified by both column chromatographic and recrystallization techniques. Chromatography was performed using either silica gel (60–120, 100–200 and 230–400 mesh) or neutral aluminum oxide. Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel $60F_{254}$). Infrared spectra were recorded on a Perkin–Elmer Spectrum 1000 FTIR spectrometer; the spectral positions (absorption maxima) are given in wave numbers (cm^{-1}). NMR spectra were recorded using Bruker AMX-400 (400 MHz) spectrometer. For ^1H NMR spectra, the chemical shifts are reported in parts per million relative to $SiMe_4$ (TMS) as an internal standard and coupling constants are presented in hertz.

Elemental analysis was performed using a Eurovector model EA3000 CHNS elemental analyzer. Mass spectra were determined on a JOEL JMS-600H spectrometer in FAB$^+$ mode using 3-nitrobenzyl alcohol as a liquid matrix. The identification of mesophases and determination of phase transition temperatures were carried out using a polarizing optical microscope (POM) (Leitz DMRXP or Leica DMLP) equipped with a programmable hot stage (Melter FP90 or FP82HT). For optical textural observations the samples were placed between untreated clean glass slides; for confirmation of assignments, two differently surface-coated slides, one treated for homogeneous alignment, the other for homeotropic alignment were used. The phase transition temperatures and associated enthalpies were determined from thermograms recorded at a scanning rate of 5 °C/min on a differential scanning calorimeter (DSC) (Perkin Elmer DSC-7 with the PC system operating on Pyris software) previously calibrated using pure indium as a standard. The energy minimized space filling molecular structures of trimers were obtained using MM2 computations of CS ChemDraw3D (version 5) program.

4.2. 4-((4-Hydroxyphenylimino)methyl)benzene-1,3-diol (1)

A mixture of 2,4-dihydroxybenzaldehyde (0.69 g, 5 mmol, 1 equiv), 4-aminophenol (0.55 g, 5 mmol, 1 equiv), absolute ethanol (10 ml), and few drops acetic acid was heated to reflux for 2 h under nitrogen atmosphere. The yellow solid separated was collected by filtration and washed with hot absolute ethanol repeatedly. It was further purified by repeated recrystallization from a mixture of tetrahydrofuran and absolute ethanol (9:1) until the melting point temperature was constant. Yield: quantitative; a yellow solid [Found: C, 68.31; H, 4.62; N, 5.78. $C_{13}H_{11}NO_3$ requires C, 68.11; H, 4.84; N, 6.11.]; mp: 248–250 °C. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2986, 2359, 2305, 1603, 1422, and 1265. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.79 (s, 1H, OH), 10.12 (s, 1H, OH), 9.54 (s, 1H, OH), 8.71 (s, 1H, CH=N), 7.35 (d, *J*=8.5 Hz, 1H, Ar), 7.2 (d, *J*=8.5 Hz, 2H, Ar), 6.79 (d, *J*=8.7 Hz, 2H, Ar), 6.35 (dd, *J*=8.4, 2.1 Hz, 1H, Ar), and 6.25 (d, *J*=2.1 Hz, 1H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): 162.8, 161.8, 159.7, 156.3, 139.4, 133.9, 122.1, 115.9, 112.2, 107.6 and 102.4.

4.3. 4′-(ω-(4-Formyl-3-hydroxyphenoxy)alkoxy)biphenyl-4-carbonitriles (4a and 4b)

A mixture of 4-(ω-bromoalkoxy)-2-hydroxybenzaldehyde (5.1 mmol, 1 equiv), 4′-hydroxy-4-biphenylcarbonitrile (5.1 mmol, 1 equiv), anhydrous potassium carbonate (0.8 g, 6.1 mmol, 1.2 equiv), catalytic amount of potassium iodide, and 2-butanone (20 ml) was refluxed for 24 h. The product obtained on evaporation of solvent was poured into water and extracted with dichloromethane (2×100 ml). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. Evaporation of solvent furnished the crude product that was purified by column chromatography using silica gel (100–200 mesh). The eluent used was a mixture of dichloromethane and hexanes (1:1).

4.3.1. Compound **4a**

Yield: 77%; a white solid [Found: C, 75.59; H, 6.79; N, 3.50. $C_{28}H_{29}NO_4$ requires C, 75.82; H, 6.59; N, 3.16.]; R_f (20% EtOAc–hexanes) 0.35; mp: 137–138 °C. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2986, 1622, and 1265. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.47 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.68 (d, *J*=8.3 Hz, 2H, Ar), 7.63 (d, *J*=8.4 Hz, 2H, Ar), 7.52 (d, *J*=8.7 Hz, 2H, Ar), 7.41 (d, *J*=8.6 Hz, 1H, Ar), 6.98 (d, *J*=8.6 Hz, 2H, Ar), 6.53 (dd, *J*=8.6 Hz, 2.2 Hz, 1H, Ar), 6.41 (d, *J*=2.2 Hz, 1H, Ar), 4.02–3.99 (m, 4H, 2×OCH_2), and 1.83–1.25 (m, 12H, 6×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 194.2, 166.4, 164.5, 159.8, 145.3, 135.2, 132.5, 131.3, 128.3, 127, 119, 115.1, 110.1, 108.7, 101.1, 68.5, 68.1, 29.2, 25.9, and 25.8.

4.3.2. Compound **4b**

Yield: 75%; a white solid [Found: C, 75.88; H, 6.79; N, 3.45. $C_{29}H_{31}NO_4$ requires C, 76.12; H, 6.83; N, 3.06.]; R_f (20% EtOAc–hexanes) 0.35; mp: 112–113 °C. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2986, 1421, and 1265. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.47 (s, 1H, OH), 9.71 (s, 1H, CHO), 7.68 (d, *J*=8.3 Hz, 2H, Ar), 7.63 (d, *J*=8.4 Hz, 2H, Ar), 7.52 (d, *J*=8.7 Hz, 2H, Ar), 7.41 (d, *J*=8.6 Hz, 1H, Ar), 6.98 (d, *J*=8.6 Hz, 2H, Ar), 6.53 (dd, *J*=8.6, 2.2 Hz, 1H, Ar), 6.41 (d, *J*=2.2 Hz, 1H, Ar), 4.02–3.99 (m, 4H, 2×OCH_2), and 1.83–1.25 (m, 14H, 7×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 194.2, 166.4, 164.5, 159.8, 145.3, 135.2, 132.5, 131.3, 128.3, 127, 119, 115.1, 110.1, 108.7, 101.1, 68.5, 68.1, 29.4, 29.2, 28.9, 26, and 25.9.

4.4. 4′-(ω-(3-Hydroxy-4-((4-hydroxyphenylimino)methyl)-phenoxy)alkoxy)biphenyl-4-carbonitriles (3a and 3b)

A mixture of 4-aminophenol (0.25 mmol, 1 equiv), 4′-(ω-(4-formyl-3-hydroxyphenoxy)alkoxy)biphenyl-4-carbonitrile (**4a** or **4b**) (0.25 mmol, 1 equiv), absolute ethanol (10 ml), and few traces of acetic acid was refluxed (2 h) until the yellow solid precipitated out. The crude product obtained was collected by filtration and repeatedly washed with absolute ethanol. It was further purified by repeated recrystallization from a mixture of tetrahydrofuran–ethanol (9:1) until a constant isotropic phase transition temperature was obtained.

4.4.1. Compound **3a**

Yield: 62%; a yellow solid [Found: C, 76.83; H, 6.49; N, 4.96. $C_{34}H_{34}N_2O_4$ requires C, 76.38; H, 6.41; N, 5.24.]; IR (KBr pellet): ν_{max} in cm^{-1} 2975, 2860, 1615, 1494, and 1217. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.87 (s, 1H, OH), 9.55 (s, 1H, OH), 8.82 (s, 1H, CH=N), 7.85 (d, *J*=8.5 Hz, 2H, Ar), 7.81 (d, *J*=8.6 Hz, 2H, Ar), 7.67 (d, *J*=8.7 Hz, 2H, Ar), 7.43 (d, *J*=8.6 Hz, 1H, Ar), 7.23 (d, *J*=8.7 Hz, 2H, Ar), 7.03 (d, *J*=8.8 Hz, 2H, Ar), 6.8 (d, *J*=8.7 Hz, 2H, Ar), 6.49 (dd, *J*=8.6, 2.3 Hz, 1H, Ar), 6.42 (d, *J*=2.3 Hz, 1H, Ar), 4.33–3.40 (m, 4H, 2×OCH_2), and 2.66–1.02 (m, 12H, 6×CH_2).

4.4.2. Compound **3b**

Yield: 64%; a yellow solid [Found: C, 77.05; H, 6.51; N, 4.98. $C_{35}H_{36}N_2O_4$ requires C, 76.62; H, 6.61; N, 5.11.]. IR (KBr pellet): ν_{max} in cm^{-1} 2975, 2862, 1618, 1495, and 1217. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.87 (s, 1H, OH), 9.55 (s, 1H, OH), 8.82 (s, 1H, CH=N), 7.86 (d, *J*=8.3 Hz, 2H, Ar), 7.81 (d, *J*=8.4 Hz, 2H, Ar), 7.68 (d, *J*=8.1 Hz, 2H, Ar), 7.44 (d, *J*=8.7 Hz, 1H, Ar), 7.24 (d, *J*=9.3 Hz, 2H, Ar), 7.05 (d, *J*=9.3 Hz, 2H, Ar), 6.80 (d, *J*=9.9 Hz, 2H, Ar), 6.52 (dd, *J*=8.6, 2.3 Hz, 1H, Ar), 6.47 (d, *J*=2.3 Hz, 1H, Ar), 4.33–3.40 (m, 4H, 2×OCH_2), and 2.66–1.02 (m, 14H, 7×CH_2).

4.5. 4′-(ω-(4-(4-(ω-(4′-cyanobiphenyl-4-yloxy)alkoxy)-2-hydroxybenzylideneamino)phenoxy)-alkoxy)biphenyl-4-carbonitriles (T-*n* series)

A mixture of 4-(ω-bromoalkoxy)biphenyl-4-carbonitrile (**2a**–**j**) (1 mmol, 2 equiv), 4-((4-hydroxyphenylimino)-methyl)benzene-1,3-diol (**1**) (0.5 mmol, 1 equiv), anhydrous potassium carbonate (2 mmol, 2 equiv), and 2-butanone (20 ml) was refluxed under N_2 atmosphere for 24 h. The reaction mixture was filtered and evaporation of 2-butanone from the filtrate furnished a yellow colored mass. The crude trimer thus obtained was purified by repeated recrystallization from a mixture of tetrahydrofuran and ethanol (9:1) until a yellow solid with a constant isotropic phase transition temperature was obtained.

4.5.1. Compound ***T-3***

Yield: 80%; a yellow solid [Found: C, 76.86; H, 4.93; N, 5.67. $C_{45}H_{37}N_3O_3$ requires C, 77.23; H, 5.33; N, 6.00.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2928, 1616, and 1265. UV–vis: λ_{max}=304.9 nm, $\varepsilon=2.1\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.87 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.1 Hz, 4H, Ar), 7.63 (d, J=8.2 Hz, 4H, Ar), 7.53 (d, J=8.7 Hz, 4H, Ar), 7.24–7.20 (m, 3H, Ar), 7.02 (d, J=8.3 Hz, 4H, Ar), 6.95 (d, J=8.7 Hz, 2H, Ar), 6.52–6.47 (m, 2H, Ar), 4.26–4.18 (m, 8H, 4×OCH_2), and 2.34–2.27 (m, 4H, 2×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.7, 162.9, 159.6, 159.5, 158, 145.3, 141.0, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 64.5, 29.3, and 29.1. MS (FAB$^+$): m/z calcd for $C_{45}H_{38}N_3O_3$ (M+1): 700.0; found: 700.2.

4.5.2. Compound ***T-4***

Yield: 81%; a yellow solid [Found: C, 77.60; H, 5.28; N, 5.71. $C_{47}H_{41}N_3O_3$ requires C, 77.56; H, 5.63; N, 5.77.]; IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2928, 1610, and 1265. UV–vis: λ_{max}=297.3 nm, $\varepsilon=0.76\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.92 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.1 Hz, 4H, Ar), 7.63 (d, J=8.2 Hz, 4H, Ar), 7.52 (d, J=8.7 Hz, 4H, Ar), 7.22–7.20 (m, 3H, Ar), 6.98 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.48–6.44 (m, 2H, Ar), 4.04–3.99 (m, 8H, 4×OCH_2), and 2.01–1.38 (m, 8H, 4×CH_2). MS (FAB$^+$): m/z calcd for $C_{47}H_{42}N_3O_3$ (M+1): 728.3; found: 728.7.

4.5.3. Compound ***T-5***

Yield: 80%; a yellow solid [Found: C, 77.91; H, 6.31; N, 5.33. $C_{49}H_{45}N_3O_3$ requires C, 77.86; H, 6.00; N, 5.56.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2942, 1606, and 1265; UV–vis: λ_{max}=294 nm, $\varepsilon=1.7\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.9 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.69 (d, J=8.2 Hz, 4H, Ar), 7.64 (d, J=8.3 Hz, 4H, Ar), 7.53 (d, J=8.6 Hz, 4H, Ar), 7.24–7.17 (m, 3H, Ar), 6.96 (d, J=8.4 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.48–6.44 (m, 2H, Ar), 4.01–3.99 (m, 8H, 4×OCH_2), and 1.85–1.38 (m, 12H, 6×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 163.2, 159.8, 159.5, 158, 145.3, 141, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 68.2, 29.2, and 25.9. MS (FAB$^+$): m/z calcd for $C_{49}H_{45}N_3O_3$: 755.3; found: 755.6.

4.5.4. Compound ***T-6***

Yield: 77%; a yellow solid [Found: C, 78.26; H, 6.85; N, 5.13. $C_{51}H_{49}N_3O_3$ requires C, 78.14; H, 6.30; N, 5.36.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2940, 1625, and 1265. UV–vis: λ_{max}=293.9 nm, $\varepsilon=1.3\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.9 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.3 Hz, 4H, Ar), 7.63 (d, J=8.4 Hz, 4H, Ar), 7.52 (d, J=8.7 Hz, 4H, Ar), 7.22–7.20 (m, 3H, Ar), 6.99 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.49–6.44 (m, 2H, Ar), 4.01–3.99 (m, 8H, 4×OCH_2), and 1.85–1.38 (m, 16H, 8×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 163.2, 159.8, 159.5, 158.0, 145.3, 141, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 68.1, 29.1, and 25.9. MS (FAB$^+$): m/z calcd for $C_{51}H_{49}N_3O_3$: 782.4; found: 782.8.

4.5.5. Compound ***T-7***

Yield: 81%; a yellow solid [Found: C, 78.31; H, 6.37; N, 5.29. $C_{53}H_{53}N_3O_3$ requires C, 78.39; H, 6.58; N, 5.17.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2937, 1605, and 1265. UV–vis: λ_{max}=293.9 nm, $\varepsilon=2.1\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.01 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.1 Hz, 4H, Ar),7.63 (d, J=8.2 Hz, 4H, Ar), 7.52 (d, J=8.6 Hz, 4H, Ar), 7. 23–7.16 (m, 3H, Ar), 6.98 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.48–6.45 (m, 2H, Ar), 4.10–3.97 (m, 8H, 4×OCH_2), and 1.83–1.25 (m, 20H, 10×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 163.2, 159.8, 159.5, 158, 145.3, 141, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 68.1, 29.2, and 26. MS (FAB$^+$): m/z calcd for $C_{53}H_{53}N_3O_3$: 812.0; found: 812.7.

4.5.6. Compound ***T-8***

Yield: 79%; a yellow solid [Found: C, 78.90; H, 6.61; N, 4.80. $C_{55}H_{57}N_3O_3$ requires C, 78.64; H, 6.84; N, 5.00.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2940, 1600, and 1265. UV–vis: λ_{max}=303.3 nm, $\varepsilon=1.3\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.9 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.3 Hz, 4H, Ar), 7.63 (d, J=8.4 Hz, 4H, Ar), 7.51 (d, J=8.7 Hz, 4H, Ar), 7.24–7.21 (m, 3H, Ar), 6.97 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.8 Hz, 2H, Ar), 6.49–6.45 (m, 2H, Ar), 4.06–4.01 (m, 8H, 4×OCH_2), and 1.89–1.56 (m, 24H, 12×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 163.2, 159.8, 159.5, 158, 145.3, 141, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 67.2, 29.7, 28.9, and 22.7. MS (FAB$^+$): m/z calcd for $C_{55}H_{57}N_3O_3$: 839.0; found: 839.1.

4.5.7. Compound ***T-9***

Yield: 79%; a yellow solid [Found: C, 78.37; H, 6.94; N, 5.03. $C_{57}H_{61}N_3O_3$ requires C, 78.86; H, 7.08; N, 4.84.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2932, 1610, and 1265. UV–vis: λ_{max}=301.9 nm, $\varepsilon=0.25\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.91 (s, 1H, OH), 8.49 (s, 1H, CH=N), 7.68 (d, J=8.3 Hz, 4H, Ar), 7.63 (d, J=8.2 Hz, 4H, Ar), 7.52 (d, J=8.7 Hz, 4H, Ar), 7.22–7.19 (m, 3H, Ar), 6.98 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.48–6.44 (m, 2H, Ar), 4.02–3.96 (m, 8H, 4×OCH_2), and 1.84–1.38 (m, 28H, 14×CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 163.8, 163.2, 159.8, 159.5, 158, 145.3, 141, 133.2, 132.6, 131.4, 128.4, 127.1, 122, 119.1, 115.2, 113.2, 110.1, 107.4, 101.7, 68.2, 29.4, 29.2, and 26.0. MS (FAB$^+$): m/z calcd for $C_{57}H_{61}N_3O_3$: 868.1; found: 868.1.

4.5.8. Compound ***T-10***

Yield: 79%; a yellow solid [Found: C, 79.15; H, 7.26; N, 4.81. $C_{59}H_{65}N_3O_3$ requires C, 79.07; H, 7.31; N, 4.69.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2854, 1605, and 1265. UV–vis: λ_{max}=299.3 nm, $\varepsilon=0.9\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.01 (s, 1H, OH), 8.46 (s, 1H, CH=N), 7.69 (d, J=8.0 Hz, 4H, Ar), 7.64 (d, J=8.0 Hz, 4H, Ar), 7.53 (d, J=8.0 Hz, 4H, Ar), 7.28–7.26 (m, 3H, Ar), 6.99 (d, J=8.3 Hz, 4H, Ar), 6.92 (d, J=8.7 Hz, 2H, Ar), 6.52–6.50 (m, 2H, Ar), 4.01–3.99 (m, 8H, 4×OCH_2), and 1.82–1.35 (m, 32H, 16×CH_2). MS (FAB$^+$): m/z calcd for $C_{59}H_{65}N_3O_3$: 896.2; found: 896.4.

4.5.9. Compound ***T-11***

Yield: 79%; a yellow solid [Found: C, 79.33; H, 7.49; N, 4.76. $C_{61}H_{69}N_3O_3$ requires C, 79.27; H, 7.53; N, 4.55.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2922, 1605, and 1265. UV–vis: λ_{max}=301.2 nm, $\varepsilon=1.14\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.91 (s, 1H, OH), 8.42 (s, 1H, CH=N), 7.61 (d, J=8.2 Hz, 4H, Ar), 7.56 (d, J=8.3 Hz, 4H, Ar), 7.45 (d, J=8.6 Hz, 4H, Ar), 7.19–7.13 (m, 3H, Ar), 6.92 (d, J=8.6 Hz, 4H, Ar), 6.84 (d, J=8.7 Hz, 2H, Ar), 6.40–6.38 (m, 2H, Ar), 3.94–3.67 (m, 8H, 4×OCH_2), and 1.78–1.25 (m, 36H, 18×CH_2). MS (FAB$^+$): m/z calcd for $C_{61}H_{69}N_3O_3$: 924.2; found: 924.5.

4.5.10. Compound ***T-12***

Yield: 78%; a yellow solid [Found: C, 79.28; H, 7.27; N, 4.81. $C_{63}H_{73}N_3O_3$ requires C, 79.46; H, 7.73; N, 4.41.]. IR (KBr pellet): ν_{max} in cm^{-1} 3054, 2918, 1603, and 1265. UV–vis: λ_{max}=302.1 nm, $\varepsilon=1.3\times10^9$ L mol^{-1} cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.91 (s, 1H, OH), 8.41 (s, 1H, CH=N), 7.67 (d, J=8.4 Hz, 4H, Ar), 7.63 (d, J=8.4 Hz, 4H, Ar), 7.53 (d, J=8.8 Hz, 4H, Ar), 7.22–7.20 (m, 3H, Ar), 6.99 (d, J=8.4 Hz, 4H, Ar), 6.92 (d, J=8.8 Hz, 2H, Ar), 6.48–6.44 (m, 2H, Ar), 4.04–3.95 (m, 8H, 4×OCH_2), and 1.85–1.38 (m, 40H, 20×CH_2). MS (FAB$^+$): m/z calcd for $C_{63}H_{73}N_3O_3$: 952.2; found: 952.4.

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