Synthesis and characterization of novel cholesterol based mesogenic compounds using 'click' chemistry

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An efficient route for the synthesis of hitherto unreported non-symmetric dimesogens consisting of a cholesteryl moiety and an aromatic mesogenic unit interconnected through a pentamethylene or decamethylene spacer by Cu(I)-catalyzed azide–alkyne cycloaddition 'click' chemistry has been developed. The aromatic units consist of two phenyl rings linked to a triazole moiety. A new trimesogen consisting two cholesteryl esters and an aromatic segment joined by pentamethylene spacer has also been synthesized. The newly synthesized mesogens show N*, TGB and partially bilayered SmC* (SmC_d*) phases. The liquid crystalline phases were investigated with the help of polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction studies. DFT study was also used to locate the orientation of the dipole at the centre position *i.e.* at ester linkage. All the compounds were characterized from their elemental analyses and spectral data.

Dimesogenic compounds (twins) consisting of two different mesogenic units interlinked through a central spacer are a relatively new class of liquid crystalline (LC) compounds that still require more intensive research in order to establish the relationship between their structure and LC properties.[1–9] Among different LC phases, the SmC phase can be obtained only by cooling three types of liquid crystalline phases—the nematic, SmA and SmD phases. Therefore, it can only inherit different textures from the aforesaid phases and should exhibit the schlieren texture. The texture obtained from the SmA phase is either schlieren or focal conic fan. Recently we have reported some unique LC properties of several different types of dimesogenic compounds and some of them showing different smectic phases.[10] Nonsymmetric dimers derived from naturally occurring cholesterol represent an exemplary and emerging class of chiral liquid crystals. These contain a cholesteryl moiety and another aromatic mesogen such as Schiff's base,[9a] azobenzene,[9b] stilbene,[11] aromatic ester,[12] or tolane unit.[9c] Here we report a unique class of cholesterol dimers where the aromatic mesogens are derived from Cu(I)-catalyzed azide–alkyne cycloaddition 'click' chemistry.

The new dimesogens **8a–d** and trimesogen **11** were synthesized starting from azides **6a,b**. These key intermediates were obtained by diazotization of the amines **5a,b** in tetrafluoroboric acid (40% solution in water) with dropwise addition of sodium nitrite (solution in water) at 0 to −5 °C and stirring for 1 h. Sodium azide was added to the methanolic solution of the diazotized salt and stirred for 1 h at rt to give azido derivatives **6a,b** in 70–75% yields. The compounds **5a,b** were prepared by the reduction of nitro derivatives **4a,b** using $SnCl_2{\cdot}2H_2O$ and refluxing in EtOAc for 5–6 h. The nitro derivatives **4a,b** were in turn prepared using earlier published standard protocol.[13] The dimesogens **8a–d** were obtained in 90–95% yields by stirring azides **6a,b** and alkynes **7a–c** in the presence of a catalytic amount of CuI in DMSO at 60 °C for 2 h (Scheme 1). The trimesogen **11** was obtained by the condensation of the amine **9** with aldehyde **10**. The amine **9** was in turn obtained by the reduction of dimesogen **8d** with $SnCl_2{\cdot}2H_2O$ in refluxing EtOAc for 2 h (Scheme 2).

The transition temperatures and the associated enthalpy values obtained from DSC for compounds **8a–d** and **11** are summarized in Table 1. The TGB transitions were not detected in DSC thermogram as their enthalpy change is very low.

Textural analysis was performed with the help of a polarizing optical microscope (POM). The dimesogens **8a–d** show the phase sequence Cr–SmC*–TGB–N*–I. On cooling the isotropic phase of the compound **8a**, a cholesteric phase with the characteristic fingerprint texture and oily streak texture was observed after shearing the sample on a glass plate. On further cooling, a TGB phase appeared over a very short temperature interval of about ~0.5 °C before transforming into SmC* phase. The SmC* phase appears as a typical fan-shaped texture[14,15] when placed in a thin cell with a cell gap of $d = 5 \pm 0.2$ μm under homogeneous planar boundary conditions. On cooling the isotropic liquid, the SmC* phase forms a fan-shaped texture which is more reminiscent of a SmC* phase than of a SmA* phase (Fig. 1a). Fig. 1b illustrates the transition from TGB to SmC* phase as the temperature is lowered from cholesteric phase. The other dimesogenic compounds **8b–d** show the same phase sequence.

The trimesogen **11**, with two cholesteryl ester units was designed and synthesized to study the stability of the SmC* phase. Optical observation of the trimesogen **11** shows a cholesteric phase in association with a TGB phase.[16] This observation is in complete agreement with the available data in the literature[17] which indicates that the TGB phase is stabilized in compounds which are highly chiral. The specific rotation measurements of the di- and trimesogens were carried out to exhibit the following results: $[\alpha]_D = -20.578$ (*c* 0.90 in $CHCl_3$)

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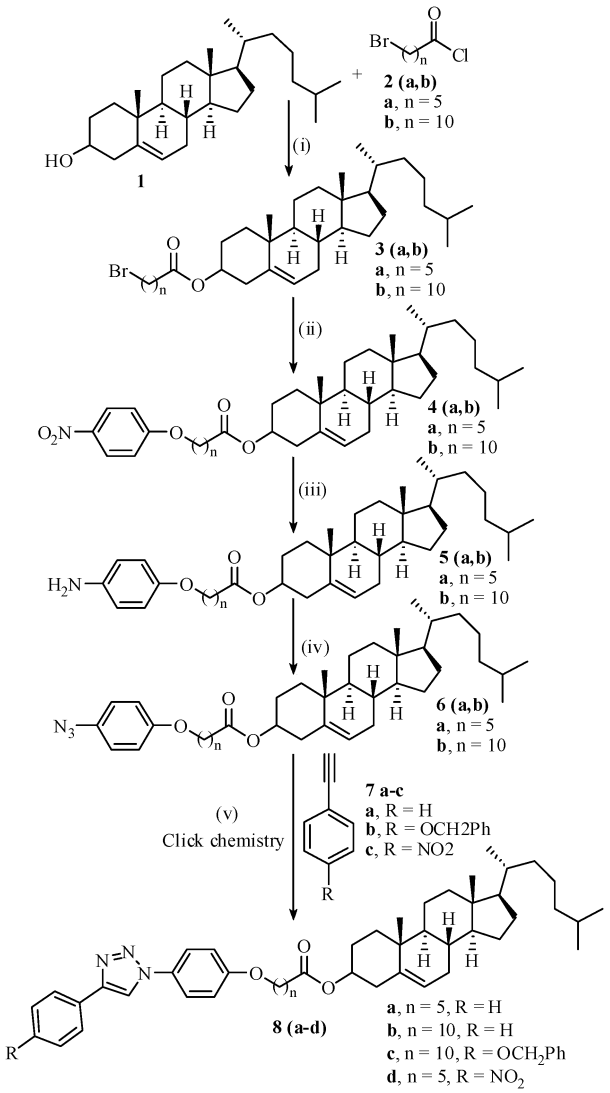
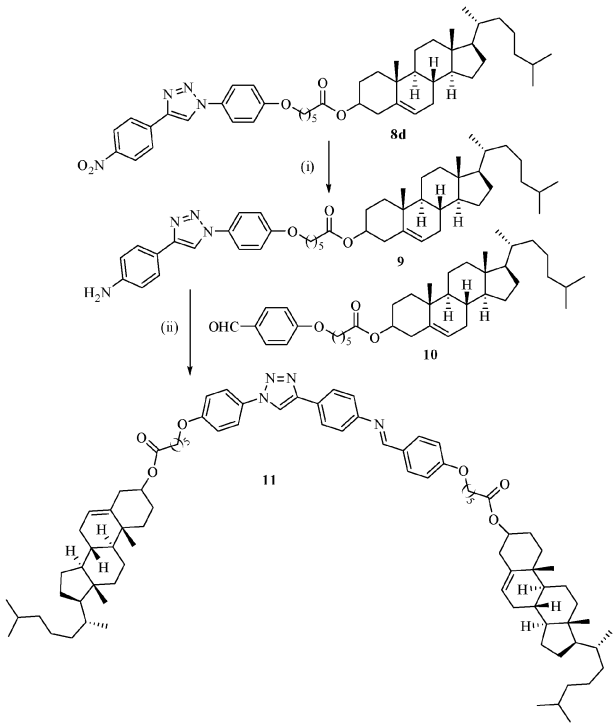


Scheme 1 Synthesis of dimesogens **8a–d**. *Reagents and conditions*: (i) THF, pyridine, rt, 12 h; (ii) *p*-nitrophenol, acetone, reflux, 12 h; (iii) $SnCl_2{\cdot}2H_2O$, EtOAc, reflux, 5–6 h; (iv) HBF_4, $NaNO_2$, NaN_3, 1 h; (v) CuI, DMSO, 60 °C, 2 h.



Scheme 2 Synthesis of trimesogen **11**. *Reagents and conditions*: (i) $SnCl_2{\cdot}2H_2O$, EtOAc, reflux, 2 h; (ii) AcOH, EtOH, reflux, 12 h.

for **8a**, −20.92 (*c* 1.00 in $CHCl_3$) for **8b**, −15.0 (*c* 0.40 in $CHCl_3$) for **8c**, −16.44 (*c* 1.08 in $CHCl_3$) for **8d** and −21.959 (*c* 0.98 in $CHCl_3$) for trimesogen **11**. The appearance of SmC* phase in trimesogen **11** is somehow different from the dimesogens and equidistant stripes were observed in the focal conic fans. The appearance of equidistance stripes in the focal conic fans is one of the important signatures of SmC* phase. Fig. 2 illustrates the polarizing optical micrograph (POM) of dimesogens **8b–d** and trimesogen **11**.

The X-ray diffraction pattern of the compound **8a** shows two sharp peaks at $\theta = 0.9586°$ ($d' = 46.07$ Å) and another reflection at $\theta = 2.496°$ ($d = 17.7$ Å). The second peak corresponding to *d* spacing of 17.7 Å may be due to the second order transition from nematic to SmC as the intensity is very weak compared to the first peak at low angle region. The fairly sharp diffuse scattering at wide angle lamellar distance of 4.5 Å corresponds to an in-layer short-range liquid-like order (Fig. 3).

From the powder X-ray diffraction pattern it is difficult to distinguish the SmC phase, where the director is tilted with respect to layer normal from that of the SmA phase. The only difference is that the layer spacing would be reduced due to the tilt in the SmC phase. From the molecular modelling of the compound **8a**, the molecular length (*L*) was calculated as 33.05 Å. The approximate *d*/*L* ratio is 1.4 and hence the smectic C phase appeared as partially bilayer in nature and designated as SmC_d. The schematic representation is shown in Fig. 4. The non-cooperative tilt angle θ_t can be deduced from molecular length *L* and *d*-spacing as the molecules are arranged in a partially bilayered fashion within *d*-spacing and found to be ~45° ($\theta_t = 44.1°$). We know that if SmC undergoes a transition directly to the nematic phase, θ_t is generally found to be temperature independent and usually about 45°.[18]

The position of the permanent dipole is important in determining the contribution of the anisotropic part of the induction forces. van der Meer and Vertogen[19] concluded that an acentral dipole, particularly an acentral transverse dipole is very important in the thermal stability of the SmC* phase. It is suggested that there is an optimal location for this dipole in the molecule, *i.e.*, the alignment of the induced and permanent dipoles creates the force for tilting the resistance to tilt. This is being contributed to by a combination of van der Waal's forces and hard core repulsions. To show the stability of SmC* phase several models were considered where the electrostatic or steric interactions were taken into account.[20,21] Besides these models Goossens[22] and other authors[23,24] developed theoretical models as molecular tilt is an intrinsic property of any layered quadrupolar structure. Strong quadrupolar moments due to acentral transverse dipoles ('outboard' dipoles) play an important role in the stabilization of the SmC* phase.

Table 1 Phase transition temperature/°C (ΔH/kJ mol^{-1})[a]

Compound	Heating	Cooling
8a	Cr 178.2(45.2) SmC* 182.3(30.1) N* 208.9(3.7) I	I 205.5(3.5) N* 175.3(19.1) SmC* 169.3(21.5) Cr
8b	Cr 130.5(53.4) SmC* 135.8(0.5) N* 153.1(1.4) I	I 152.4(1.3) N* 134.9(0.7) SmC* 115.9(50.9) Cr
8c	Cr 90.5(15.6) SmC* 134.7(5.2) N* 156.1(0.3) I	I 146.5(2.3) N* 129.5(5.9) SmC* 126.4(9.4) 88.2(19.1) Cr
8d	Cr 115.1(2.1) SmC* 124.5(32.3) N* 134.9(1.4) I	I 134.4(1.5) LC phase
11	Cr 162.7(37.2) SmC* 180.3(26.2) N* 238.1(3.3) I	I 228.9(4.9) N* 173.7 (13.1) SmC* 159.9(20.7) Cr

[a] TGB transition temperatures were not detected in DSC thermogram as their enthalpy change is very low.

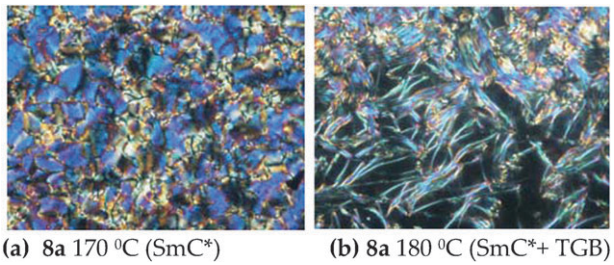


Fig. 1 POM micrograph of **8a**.

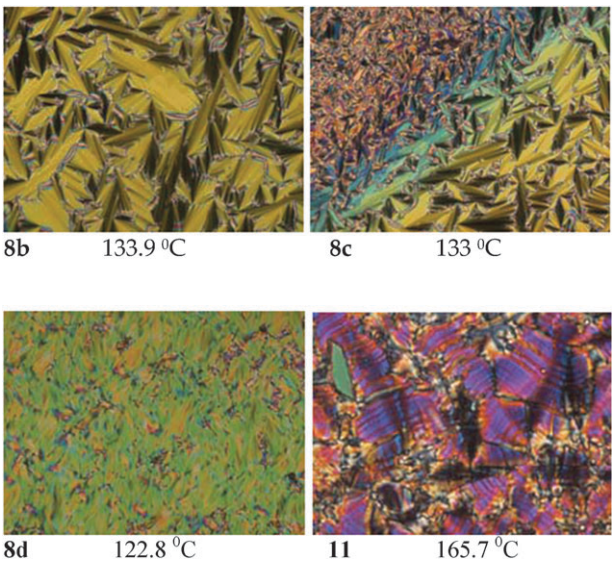


Fig. 2 Polarizing micrograph of SmC* phases of compounds **8b–d** and **11** at different temperatures.

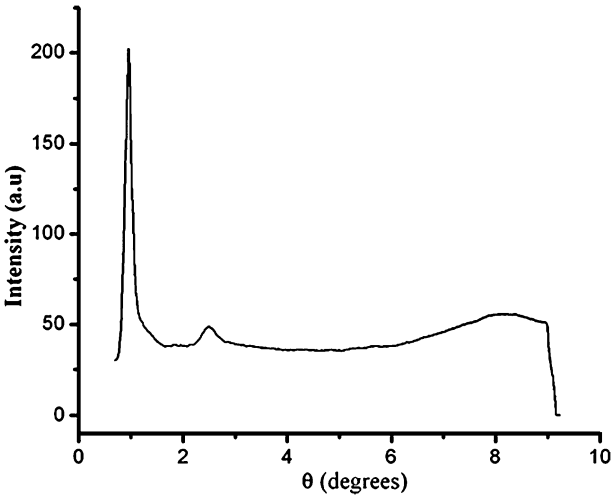


Fig. 3 X-Ray diffraction pattern of compound **8a** at 175 °C.

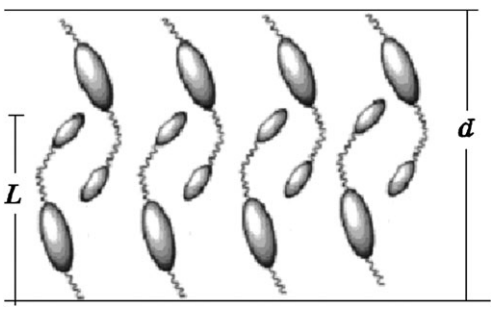


Fig. 4 Schematic representation of partially bilayer SmC phase deduced from powder X-ray pattern.

The direction of the dipole of the compound **8a** was calculated by Density Functional Theory (DFT), which may determine the presence of dipolar interaction within the molecules. All calculations have been performed by the Chem3D (version 10)[25] with GAUSSIAN 03 Interface.[26] We have computed the DFT (B3LYP) level of theory using the basis set 6-31G to obtain the dipole moment and dipolar orientation of molecules. The dipole moment of **8a** has been calculated as 8.9106 D (X = −7.4802, Y = −4.2888, Z = 2.2478). Geometry optimization of the compound **8a** was performed by addition of atoms step by step. The optimized structure suggests that the molecule is completely rod in shape (Fig. 5).

First optimization was conducted by MM2 method followed by AM1 method and finally DFT was performed as stated earlier. From the calculated value of the dipole moment it is found that the maxima of the dipole is in the direction of negative X-axis, and if we suppose Z-axis as a molecular axis then the direction of maxima of the dipole is along the negative of X-axis which is centrally transverse and this is a favorable condition for the appearance of SmC phase, in which a permanent dipole in one molecule induces a dipole in a neighboring molecule. The alignment of the induced and the permanent dipoles that creates the force to tilt and the associated tilting is being contributed by a combination of van der Waal's forces and hard core repulsions, where the molecules are allowed to rotate freely and flexible enough to make allowances for changes in molecular structure.

Fig. 6 illustrates the optimized structure of the compound **8a** and the geometry optimization was done at the central part (at oxygen atom of ester linkage) of the molecule. To find out the dipole moment and the direction of dipole at central part we carried out a DFT calculation and found it to be 8.0968 D (X = −6.8656, Y = −3.9197, Z = 1.7487). Here again we

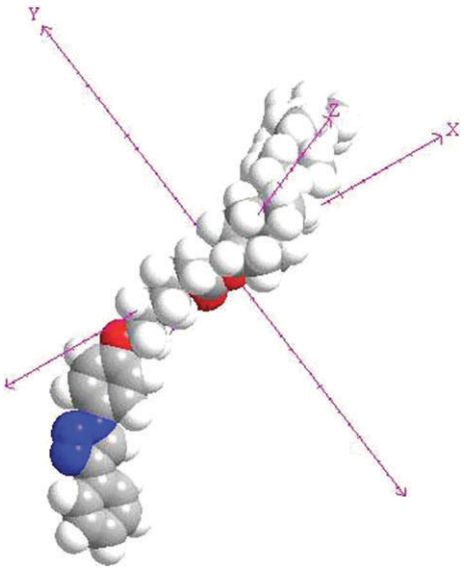


Fig. 5 Optimized geometry of **8a** from DFT study. Direction of central dipole is clearly visible along negative of the *X*-axis.

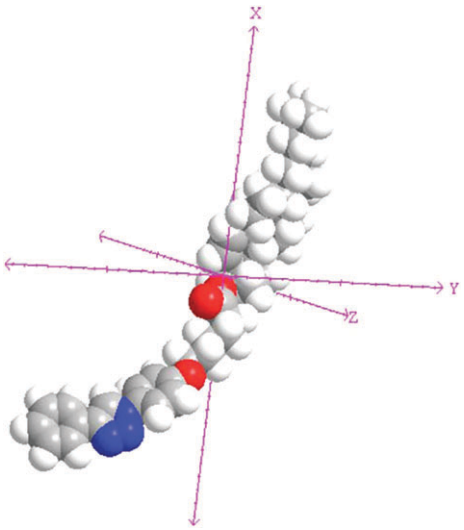


Fig. 6 Central part optimized geometry of compound **8a** and direction of dipole is outboard transverse (negative direction of *X*-axis).

observed that the direction of the dipole moment is outboard transverse *i.e.* along the negative direction of the *X*-axis with slight decrease in total dipole moment of the whole molecule. Central location of dipole may be responsible for determining the direction of dipole of the molecule itself.

It is a well known fact that the terminal branched chain can often stabilize the existence of SmC phase. However, in our case there is no terminal branched chain at one end but if we consider the terminal branched chain of the cholesteryl moiety (2,6-dimethylheptane) there is a chance of exhibiting SmC* phase. As discussed above we have not observed schlieren texture of SmC* phase on the cooling cycle, only the broken focal conic fans were observed[27] and that is quite possible where only broken focal conic fans appear.

In conclusion, we have developed a new and efficient route for the synthesis of new di- and trimesogenic compounds containing cholesteryl moiety by Cu(I)-catalyzed azide–alkyne cycloaddition 'click' chemistry. To the best of our knowledge so far, there is only one report of cholesterol based liquid crystal using 'click' chemistry.[28] The newly synthesized mesogenic compounds show SmC* phase along with TGB and cholesteric phase. The mesophases were characterized with the help of polarizing optical microscopy, DSC, powder X-ray diffraction pattern and some computational study. From DFT study of the central part of molecule (at oxygen atom), it has been shown that the outboard transverse dipole has a crucial role in stabilizing the SmC* phase. The branched chain of the rigid cholesteryl part also plays an important role in stabilizing the SmC* phase.

Experimental

General

All the chemicals were procured from either Sigma Aldrich Chemicals Pvt. Ltd. or Spectrochem, India. Silica gel (60–120 mesh) was used for chromatographic separation. Silica gel G [E-Merck (India)] was used for TLC. Petroleum ether refers to the fraction boiling between 60 °C and 80 °C. IR spectra were recorded on a Perkin-Elmer L 120-000A spectrometer (ν_{max} in cm^{-1}) on KBr disks. ^1H NMR (400 MHz) spectra were recorded on a Bruker DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with TMS as internal standard. ^{13}C-NMR spectra were determined for solutions in $CDCl_3$ on a Bruker DPX-75. CHN was recorded on a Perkin Elmer 2400 series II CHN analyzer. The liquid crystalline properties were established by thermal microscopy (Nikon polarizing microscope LV100POL attached with Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302) and the phase transitions were confirmed by differential scanning calorimetry (Perkin-Elmer DSC Pyris1 system). X-Ray diffraction was carried out on a Philips powder diffractometer (PAN analytical model no. PW 3015) operating on X'pert pro software, equipped with a temperature controller permitting low as well as high temperature operation as needed (with CuKα radiation of λ = 1.5418 Å).

General procedure for the synthesis of azido derivatives 6a,b

To a magnetically well-stirred mixture of the amine **5a** (500 mg, 0.845 mmol) in tetrafluoroboric acid (40% solution in water, 5 mL), a solution of $NaNO_2$ (116.68 mg, 1.69 mmol) in water (2 mL) was added drop wise at 0 to −5 °C and stirring was continued for 1 h. The solid diazonium salt was filtered and dried. The solid salt was then taken in dry MeOH (10 mL) and sodium azide (109.9 mg, 1.69 mmol) was added all at once at ice cool condition. After stirring for 1 h at rt, the solvent was removed *in vacuo* and the residue was extracted with Et_2O (3 × 30 mL) and the ether extract was washed with water (20 mL), dried (Na_2SO_4) and concentrated to afford the azido derivative **6a** as white solid. The other amine compound **5b** (500 mg, 0.755 mmol) was similarly treated to afford product **6b**.

Compound 6a. Yield (391 mg) 75%; mp 88–90 °C. IR (KBr): 2948, 2109, 1726, 1505, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.32 (m, 51H), 3.92 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 4.0 Hz, 1H), 6.85

(d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 21.2, 22.7, 23.0, 24.0, 24.4, 24.9, 25.7, 28.0, 28.1, 28.4, 29.1, 32.0, 32.1, 34.7, 35.9, 36.3, 36.7, 37.1, 38.3, 39.7, 39.9, 42.4, 50.2, 56.3, 56.8, 68.2, 74.0, 115.9, 120.1, 122.8, 132.3, 139.8, 156.6, 173.1. Anal. calcd. for $C_{39}H_{59}N_3O_3$: C, 75.81; H, 9.62; N, 6.80%. Found: C, 75.94; H, 9.69; N, 6.72%.

Compound 6b. Yield (364 mg) 70%; mp 70–72 °C. IR (KBr): 2919, 2113, 1736, 1504, 1237 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.30 (m, 61H), 3.91 (t, J = 6.6 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 3.6 Hz, 1H), 6.86 (d, J = 9.0 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 25.2, 26.0, 26.1, 28.0, 28.1, 28.4, 29.1, 29.2, 29.3, 29.4, 29.5, 29.5, 29.6, 29.6, 32.0, 32.1, 34.8, 35.9, 36.3, 36.7, 37.2, 38.3, 39.7, 39.9, 42.5, 50.2, 56.3, 56.8, 68.6, 69.2, 73.9, 110.9, 115.9, 120.1, 121.7, 122.0, 122.7, 132.3, 139.9, 156.7, 173.4. Anal. calcd. for $C_{44}H_{69}N_3O_3$: C, 76.81; H, 10.11; N, 6.11%. Found: C, 76.68; H, 10.21; N, 6.17%.

General procedure for the synthesis of dimesogenic compounds 8a–d by 'click' chemistry

To a well-stirred solution of the azides **6a,b** (0.285 mmol) and alkynes **7a–c** (0.428 mmol) in DMSO (10 mL), catalytic amount (10 mol%) of CuI (I) was added and stirred for 2 h at 60 °C. After cooling the reaction mixture was poured into water (100 mL) and extracted with $CHCl_3$ (3 × 30 mL). The organic layer was washed with water (20 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated under vacuum. The crude product was purified by column chromatography over silica gel using (1 : 1) ethyl acetate : petroleum ether as eluent, which afforded the dimesogenic compounds **8a–d** in 90–95% yields.

Compound 8a. Yield (195 mg) 95%; IR (KBr): 2939, 1731, 1524, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.32 (m, 51H), 4.00 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 6.9 Hz, 1H), 7.44 (t, J = 6.9 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 8.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 18.7, 19.3, 21.0, 22.5, 22.8, 23.8, 24.2, 24.7, 25.5, 27.8, 28.0, 28.2, 28.8, 31.8, 31.9, 34.5, 35.7, 36.1, 36.5, 36.9, 38.1, 39.5, 39.7, 42.2, 49.9, 56.1, 56.6, 68.0, 73.8, 115.2, 117.8, 122.1, 122.6, 125.8, 128.3, 128.9, 130.3, 139.6, 148.1, 159.3, 173. $[\alpha]_D$ −20.578 (c 0.90 in $CHCl_3$). HRMS: calculated for $C_{47}H_{65}N_3O_3$: 720.5099 [M + H]. Found: 720.5078 [M + H]. Anal. calcd. for $C_{47}H_{65}N_3O_3$: C, 78.40; H, 9.10; N, 5.84%. Found: C, 78.54; H, 8.99; N, 5.95%.

Compound 8b. Yield (212 mg) 94%; IR (KBr): 2934, 1733, 1521, 1171 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.31 (m, 61H), 4.00 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 4.0 Hz, 1H), 7.01 (d, J = 8.6 Hz, 2H), 7.35 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.89 (d, J = 7.5 Hz, 2H), 8.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 18.7, 19.3, 21.0, 22.5, 22.8, 23.8, 24.2, 25.0, 26.0, 27.8, 28.0, 28.2, 29.0, 29.1, 29.2, 29.3, 29.3, 29.4, 31.8, 31.9, 34.7, 35.8, 36.1, 36.6, 37.0, 38.1, 39.5, 39.7, 42.3, 50.0, 56.1, 56.6, 68.4, 73.7, 115.3, 117.8, 122.1, 122.6, 125.8, 128.3, 128.8, 130.3, 130.4, 139.7, 148.1, 159.4, 173.3. $[\alpha]_D$ −20.92 (c 1.00 in $CHCl_3$). Anal. calcd. for $C_{52}H_{75}N_3O_3$: C, 79.04; H, 9.57; N, 5.32%. Found: C, 79.24; H, 9.65; N, 5.38%.

Compound 8c. Yield (230 mg) 90%; IR (KBr): 2933, 1734, 1517, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.28 (m, 61H), 4.00 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.06 (s, 2H), 5.36 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 7.2 Hz, 2H), 7.09 (d, J = 7.0 Hz, 4H), 7.39–7.42 (m, 6H), 7.92 (d, J = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 12.3, 19.1, 19.7, 23.0, 23.2, 24.2, 25.5, 26.4, 28.4, 28.6, 29.5, 29.7, 29.9, 32.3, 32.4, 35.1, 36.2, 37.4, 38.6, 39.9, 40.1, 42.7, 50.4, 56.6, 57.1, 68.9, 70.5, 74.1, 115.3, 115.4, 115.7, 123.0, 127.9, 128.2, 128.5, 129.0, 129.4, 140.1, 173.7. $[\alpha]_D$ −15.0 (c 0.40 in $CHCl_3$). Anal. calcd. for $C_{59}H_{81}N_3O_4$: C, 79.06; H, 9.11; N, 4.69%. Found: C, 79.18; H, 9.18; N, 4.57%.

Compound 8d. Yield (203 mg) 93%; IR (KBr): 2945, 1712, 1517 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.95 (m, 51H), 4.00 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 4.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 6.9 Hz, 2H), 7.79 (t, J = 6.9 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 8.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 21.2, 22.7, 22.9, 24.0, 24.4, 24.8, 25.7, 28.0, 28.1, 28.3, 29.0, 32.0, 32.0, 33.0, 33.2, 34.7, 35.9, 36.3, 36.7, 37.1, 38.3, 39.6, 39.8, 42.4, 50.2, 56.3, 56.8, 68.3, 115.5, 119.2, 122.4, 122.8, 123.9, 125.8, 129.0, 130.1, 135.0, 139.2, 139.8, 146.3, 148.7, 159.8, 173.1. $[\alpha]_D$ −16.44 (c 1.08 in $CHCl_3$). Anal. calcd. for $C_{47}H_{64}N_4O_5$: C, 73.79; H, 8.43; N, 7.32%. Found: C, 73.98; H, 8.48; N, 7.27%.

Synthesis of amine derivative 9

To a solution of the dimesogenic compound **8d** (250 mg, 0.327 mmol) in EtOAc (10 mL), $SnCl_2{\cdot}2H_2O$ (369 mg, 1.634 mmol) was added and refluxed for 2 h. The reaction mixture was cooled and portion wise poured into saturated bicarbonate solution. The mixture was then filtered through Celite bed and repeatedly washed with ethyl acetate. The organic layer was dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography over silica gel using 1 : 1 ethyl acetate : petroleum ether as eluent.

Compound 9. Yield (231 mg) 96%; IR (KBr): 3441, 3362, 2952, 1717, 1520, 1261 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.60 (m, 51H), 3.74 (s, 2H), 4.00 (t, J = 6.1 Hz, 2H), 4.59–4.62 (m, 1H), 5.36 (d, J = 4.0 Hz, 1H), 6.73 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.6 Hz, 2H), 7.96 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 12.3, 14.4, 19.1, 19.7, 23.0, 23.2, 24.2, 25.2, 26.0, 28.2, 28.4, 28.6, 29.3, 31.4, 31.5, 32.3, 32.4, 35.0, 36.2, 37.4, 38.6, 39.9, 42.7, 50.4, 56.5, 57.1, 68.5, 74.3, 115.7, 115.8, 116.6, 117.0, 121.9, 122.5, 123.1, 125.0, 127.6, 128.1, 131.0, 140.1, 144.0, 149.1, 159.6, 173.4. Anal. calcd. for $C_{47}H_{66}N_4O_3$: C, 76.80; H, 9.05; N, 7.62%. Found: C, 76.71; H, 9.15; N, 7.67%.

Synthesis of trimesogenic compound 11

A mixture of the compound **9** (138 mg, 0.187 mmol) and cholesteryl benzoate **10** (114 mg, 0.187 mmol) was refluxed in absolute ethanol (15 mL) in the presence of a catalytic amount of glacial acetic acid for 12 h. The trimesogen **11** was obtained

as a precipitate from the hot reaction mixture. It was repeatedly washed with hot ethanol and dried under vacuum.

Compound 11. Yield (243 mg) 98%; IR (KBr): 2946, 2867, 1732, 1517, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H = 0.66–2.81 (m, 102 H), 4.00 (t, J = 6.1 Hz, 4H), 4.59–4.62 (m, 2H), 5.36 (d, J = 4.0 Hz, 2H), 7.00 (d, J = 7.8 Hz, 6H), 7.66 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.2 Hz, 2H), 8.08 (s, 1H), 8.34 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 22.3, 22.5, 23.5, 24.0, 24.4, 25.3, 25.3, 27.5, 27.7, 27.9, 28.5, 31.1, 31.5, 31.6, 32.5, 34.2, 35.5, 35.9, 36.3, 36.7, 37.9, 39.2, 39.4, 42.0, 49.7, 55.8, 56.4, 67.5, 67.8, 73.5, 114.4, 115.0, 117.1, 118.0, 121.8, 122.3, 123.9, 126.6, 127.1, 129.2, 130.1, 130.2, 137.2, 139.3, 139.4, 148.0, 150.7, 158.2, 159.0, 161.4, 172.6, 172.7. $[\alpha]_D$ −21.959 (*c* 0.98 in $CHCl_3$). Anal. calcd. for $C_{87}H_{124}N_4O_6$: C, 79.05; H, 9.45; N, 4.24%. Found: C, 79.24; H, 9.33; N, 4.31%.

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