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Synthesis and comparative study on phase transition behavior of triazole-cored liquid crystals armed with cholesterol and double or triple aromatic rings systems

Contents

1. Techniques

All the chemicals were obtained from Sigma Aldrich Chemicals and TCI Company and used as received. The solvents were purified and dried by standard methods and the crude samples were purified by column chromatographic technique using silica gel (230-400 mesh) as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merch, Kieselgel 60, F254). The infrared (IR) spectra for all compounds were recorded in the range 400-4000 cm^{-1} using a Perkin-Elmer 2000 FTIR spectrophotometer with the samples embedded in KBr discs. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz Ultra-Shield spectrometer. $CDCl_3$ and DMSO-d_6 were used as solvents and TMS as the internal standard. CHN microanalyses were carried out on a Perkin-Elmer 2400 LS Series CHNS/O Analyzer. The liquid crystalline textures were observed under a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam TMS94 temperature controller and a LTS350 hot stage. The transition temperatures and enthalpy changes were measured by a differential scanning calorimeter TA Q200 at a rate of 5 °C min^{-1} for both heating and cooling cycles.

2. General procedure for the synthesis of intermediate and final compounds

2.1. Procedure for the synthesis of 4-azidonitrobenzene (1)

4-Nitroaniline (13.8 g, 0.1 mol) was dissolved in diluted hydrochloric acid prepared from 4 mL concentrated HCl and 10 mL water. 100 mL of water was then added and the solution was cooled to 0-5 °C in an ice-salt bath. A solution of sodium nitrite (8.3 g, 0.12 mol) in water (2 mL) was added dropwise upon stirring for 10 mins. With vigorous stirring, a solution of sodium azide (6.5 g, 0.10 mol) in water (2 mL) was added and the resulting precipitate was isolated by

filtration, washed with excess of water and dried in air. Recrystallization from hexane afforded the 4-azidonitrobenzene as yellow-colored crystals.

Yield: 95%. M. P. 69-71 °C. $C_6H_4N_4O_2$: Calc. C, 43.91; H, 2.46; N, 34.14; found C, 43.88; H, 2.49; N, 34.13. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 2125 (Ar-N_3), 1517, 1343 (Ar-NO_2), 1592 (aromatic C=C). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.49 (d, J=9.0 Hz, 2H, Ar), 7.74 (d, J=9.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$) δ/ppm: 150.1, 147.9, 129.7, 123.9.

2.2. Procedure for the synthesis of 1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylic acid (2)

To a solution of 4-azidonitrobenzene (8.2 g, 0.05 mol) and propiolic acid (3 ml, 0.05 mol) in dry THF, CuI (0.5 g, 5 mol %) was added by one portion. The reaction mixture was refluxed under N_2 atmosphere for overnight. The reaction mixture was then cooled to room temperature and filtered. The solvent was removed under vacuum to afford 1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylic acid as a yellow colored solid. The crude product was washed and recrystallized from ethanol to get pale yellow powder.

Yield: 80%. $C_9H_6N_4O_4$: Calc. C, 46.16; H, 2.58; N, 23.93; found 45.63; H, 2.52; N, 23.92. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3257 (acid -OH), 1735 (acid -C=O), 3139 (triazole C-H), 1219, 1151 (triazole -N=N-), 1517, 1344 (Ar-NO_2). ^{1}H NMR ($CDCl_3$), δ/ppm: 9.62 (s, 1H, COOH), 8.48 (d, J=9 Hz, 2H, Ar-H), 8.46 (s, 1H, triazole -CH), 8.32 (d. J=8.5 Hz, 2H, Ar-H). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.7 (-COOH), 147.9, 142.3 (triazole Ar-C), 140.5, 125.4, 123.2 (triazole Ar-C), 120.9.

2.3. Procedure for the synthesis of cholesteryl(1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate) (3)

A mixture containing compound **2** (4 g, 0.012 mol), cholesterol (4.7 g, 0.012 mol), DCC (4.1 g, 0.02 mol) and DMAP (0.07 g, 5 mol %) in dry dichloromethane (50 ml) was stirred for 12 hrs under N_2 atmosphere. Upon completion of reaction, N, N- dicyclohexylurea was filtered off, and the organic layer was washed with 3 x 200 ml of water and dried with anhydrous sodium sulphate. The solvent was removed under vacuum and purified by silica gel column chromatography using chloroform as eluent. The solid thus obtained was further recrystallized from ethanol which afforded white color powder.

Yield: 73%. $C_{36}H_{50}N_4O_4$: Calc. C, 71.73; H, 8.36; N, 9.29; found C, 71.14; H, 8.31; N, 9.32. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3121 (triazole -CH), 2945 (alkyl -CH), 1721 (ester, -C=O), 1533, 1345 (-NO_2), 1270, 1157 (triazole -N=N-). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.62 (s, 1H, triazole -CH), 8.46 (d, J=9 Hz, 2H, Ar-H), 8.04 (d, J=9 Hz, 2H, Ar-H), 4.99 (b, J=16 Hz, 1H, olefinic), 3.73 (m, 1H, -COOCH), 2.55-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.04 (m, 26H, 10 x CH_2, 6 x CH), 1.01 (s, 3H, -CH_3), 0.99 (d, J=5.5 Hz, 3H, -CH_3), 0.87 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 159.6 (ester, -C=O), 147.7, 141.9, 141.7, 139.3, 125.6, 125.4, 123.2, 120.9, 120.8, 75.7, 56.7, 56.1, 50.0, 42.3, 39.7, 38.0, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 31.1, 28.2, 28.0, 27.7, 26.1, 24.3, 23.8, 22.5, 21.0, 19.3, 18.7, 18.4, 11.8.

2.4. Procedure for the synthesis of cholesteryl(1-(4-aminophenyl)-1H-1,2,3-triazole-4-carboxylate) (4)

To cholesteryl(1-(4-nitrophenyl)-1H-1,2,3-triazole-4-carboxylate) (6 g, 0.013 mol) in ethanol (121 mL), water (34 mL), iron powder (1.1 g, 0.02 mol) and ammonium chloride (0.42g, 0.008 mol) were added and the reaction mixture was stirred at 85˚C for 1 hr, cooled to room temperature and filtered. The filtrate was concentrated to a low volume (50 mL), poured into a separating funnel with ice and 10% NaOH solution was added until a gray precipitate persisted. The aqueous layer was extracted three times with chloroform (2 x 150 mL) and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was evaporated to give compound **4** as a pale gray colored powder.

Yield 70%. $C_{36}H_{52}N_4O_2$: Calc. C, 75.48; H, 9.15; N, 9.78; found C, 75.22; H, 9.19; N, 9.75; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3418 (amine -NH), 2948 (alkyl -CH), 1722 (ester, -C=O), 1521, 1345 (-NO_2), 1265, 1157 (triazole -N=N-). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.44 (s, 1H, triazole -CH), 6.61 (d, J=8 Hz, 2H, Ar-H), 7.38 (d, J=8 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 3.73 (m, 1H, -COOCH), 2.56-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.04 (m, 26H, 10 x CH_2, 6 x CH), 1.01 (s, 3H, -CH_3), 0.99 (d, J=5.5 Hz, 3H, -CH_3), 0.88 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.69 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 159.6 (ester, -C=O), 148.4, 141.9, 139.3, 130.5, 127.1, 126.4, 126.2, 123.2, 120.8, 75.7, 56.7, 56.1, 50.0, 42.3, 39.7, 38.0, 37.0, 36.6, 36.2, 35.8, 31.9, 31.8, 31.1, 28.2, 28.0, 27.7, 26.1, 24.3, 23.8, 22.5, 21.0, 19.3, 18.7, 18.4, 11.8.

2.5. General procedure for the synthesis of compounds 6a-6g

A mixture of cholesteryl(1-(4-aminophenyl)-1H-1,2,3-triazole-4-carboxylate) (4) (0.0004 mol), 4-alkyloxybenzaldehyde (0.0004 mol) and catalytic amount of concentrated HCl (2 drops) in chloroform was refluxed for 1 h. The reaction mixture was cooled to room temperature. The solvent was removed and repeated crystallization from ethanol to get pale yellow color solid.

6a: Yield 85%. $C_{49}H_{68}N_4O_3$: Calc. C, 77.33; H, 9.01; N, 7.36; found C, 77.37; H, 9.11; N, 7.30. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic -CH), 1706 (ester -C=O), 1656 (imine –CH=N), 1594, 1527 (-NO_2), 1273, 1184 (triazole -N=N-), 1032(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.00 (d, J=6.5 Hz, 2H, Ar-H), 6.78 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, -OCH_2), 3.94 (b, 1H, -COOCH), 2.56-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.04 (m, 34H, 14 x CH_2, 6 x CH), 1.01 (s, 3H, -CH_3), 0.99 (d, J= 5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J = 2.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.8, 160.0, 152.1, 140.9, 132.9, 132.6, 129.8, 128.4, 128.0, 123.0, 122.3, 121.8, 114.5, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 39.9, 39.8, 38.5, 37.3, 37.2, 36.1, 35.8, 32.1, 31.9, 31.8, 131.1, 29.6, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.5, 21.0, 19.3, 14.1, 12.1.

6b: Yield 88%. $C_{50}H_{70}N_4O_3$: Calc. C, 77.48; H, 9.10; N, 7.23; found C, 77.51; H, 9.16; N, 7.25; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic -CH), 1705 (ester –C=O), 1656 (imine -CH=N), 1594, 1528 (-NO_2), 1273, 1185 (triazole -N=N-), 1032(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.53 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.01 (d, J=6.5 Hz, 2H, Ar-H), 6.79 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, -OCH_2), 3.94 (b, 1H, -COOCH), 2.55-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.07-2.04 (m, 36H, 15 x CH_2, 6 x CH), 1.00 (s, 3H, -CH_3), 0.99 (d, J= 5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J = 2.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.8, 160.0, 152.2, 140.9, 132.9, 132.5, 129.8, 128.4, 128.1, 123.0, 122.3, 121.8, 114.4, 73.7, 68.7, 56.5, 56.0, 50.9, 42.8, 39.9, 39.7, 38.5, 37.3, 37.1, 36.1, 35.8, 32.2, 31.9, 31.7, 31.1, 29.6, 28.6, 28.2, 27.7, 26.3, 26.1, 25.9, 25.4, 24.7, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

6c: Yield 87%. $C_{51}H_{72}N_4O_3$: Calc. C, 77.62; H, 9.20; N, 7.10; found C, 77.65; H, 9.23; N, 7.08; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic -CH), 1707 (ester -C=O), 1656 (imine –CH=N), 1594, 1527 (-NO_2), 1275, 1184 (triazole -N=N-), 1033(ether -C-O). ^{1}H NMR ($CDCl_3$),

δ/ppm: 8.54 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.01 (d, J=6.5 Hz, 2H, Ar-H), 6.78 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.04 (t, J=13.5 Hz, 2H, $-OCH_2$), 3.94 (b, 1H, -COOCH), 2.56-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.05 (m, 38H, 16 x CH_2, 6 x CH), 1.00 (s, 3H, $-CH_3$), 0.99 (d, J= 5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.8, 160.1, 152.2, 140.8, 132.9, 132.6, 129.8, 128.4, 128.1, 123.0, 122.3, 121.8, 114.4, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 39.9, 39.7, 38.5, 37.4, 37.1, 36.1, 35.8, 32.2, 31.9, 31.7, 31.1, 29.5, 28.6, 28.2, 27.7, 26.3, 26.1, 25.9, 25.4, 24.7, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

6d: Yield 81%. $C_{52}H_{74}N_4O_3$: Calc. C, 77.76; H, 9.29; N, 6.98; found C, 77.78; H, 9.28; N, 6.94; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic -CH), 1707 (ester -C=O), 1656 (imine –CH=N), 1594, 1527 ($-NO_2$), 1273, 1184 (triazole -N=N-), 1032(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.53 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.01 (d, J=6.5 Hz, 2H, Ar-H), 6.78 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, $-OCH_2$), 3.94 (b, 1H, -COOCH), 2.56-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.06 (m, 40H, 17 x CH_2, 6 x CH), 1.00 (s, 3H, $-CH_3$), 0.99 (d, J=5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.69 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.8, 160.2, 152.2, 140.6, 132.9, 132.5, 129.8, 128.6, 128.1, 123.2, 122.3, 121.8, 114.0, 73.7, 68.7, 56.5, 56.1, 50.7, 42.8, 39.9, 39.7, 38.3, 37.4, 37.1, 36.1, 35.8, 32.4, 31.9, 31.7, 31.1, 29.5, 28.6, 28.2, 27.7, 26.3, 26.1, 25.9, 25.4, 24.7, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

6e: Yield 79%. $C_{53}H_{76}N_4O_3$: Calc. C, 77.90; H, 9.37; N, 6.86; found C, 77.94; H, 9.35; N, 6.80; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic –CH), 1706 (ester -C=O), 1656 (imine –CH=N), 1594, 1527 ($-NO_2$), 1273, 1184 (triazole -N=N-), 1032(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.36 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.01 (d, J=6.5 Hz, 2H, Ar-H), 6.78 (d, J=9 Hz, 2H, Ar-H), 4.98 (brd, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, $-OCH_2$), 3.94 (brd, 1H, -COOCH), 2.56-2.64 (brd, J=7 Hz, 2H, allylic methylene), 1.05-2.04 (m, 42H, 18 x CH_2, 6 x CH), 1.01 (s, 3H, $-CH_3$), 0.99 (d, J= 5.5 Hz, 3H, CH_3), 0.92 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J = 2.5 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.7, 160.2, 152.2, 140.6, 132.9, 132.5, 129.8, 128.6, 128.2, 123.2, 122.2, 121.8, 114.0, 73.7, 68.7, 56.6, 56.1, 50.7, 42.8,

39.9, 39.7, 38.3, 37.4, 37.3, 36.1, 35.8, 32.4, 31.9, 31.7, 31.1, 29.5, 28.6, 28.2, 27.7, 26.3, 26.1, 25.9, 25.4, 24.7, 23.8, 22.5, 21.1, 19.5, 14.1, 12.1.

6f: Yield 77%. $C_{54}H_{78}N_4O_3$: Calc. C, 78.03; H, 9.46; N, 6.74; found C, 78.07; H, 9.47; N, 6.71; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3441, 2928, 2853 (aliphatic -CH), 1705 (ester -C=O), 1657 (imine –CH=N), 1595, 1527 (-NO_2), 1273, 1184 (triazole -N=N-), 1032(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.00 (d, J=6.5 Hz, 2H, Ar-H), 6.79 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, -OCH_2), 3.94 (b, 1H, -COOCH), 2.56-2.62 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.04 (m, 44H, 19 x CH_2, 6 x CH), 1.01 (s, 3H, -CH_3), 0.99 (d, J= 5.5 Hz, 3H, CH_3), 0.92 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.8, 160.0, 152.2, 140.5, 132.9, 132.5, 129.8, 128.6, 128.2, 123.2, 122.3, 121.8, 114.1, 73.7, 68.7, 56.5, 56.0, 50.7, 42.8, 39.9, 39.7, 38.3, 37.4, 37.1, 36.1, 35.8, 32.5, 31.9, 31.7, 31.1, 29.5, 28.6, 28.2, 27.8, 26.3, 26.1, 25.9, 25.4, 24.7, 23.8, 22.5, 21.2, 19.3, 14.1, 12.1.

6g: Yield 76%. $C_{55}H_{80}N_4O_3$: Calc. C, 78.15; H, 9.54; N, 6.63; found C, 78.18; H, 9.50; N, 6.67; FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3442, 2928, 2853 (aliphatic -CH), 1707 (ester -C=O), 1656 (imine –CH=N), 1594, 1528 (-NO_2), 1277, 1184 (triazole -N=N-), 1033(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 7.83 (d, J=9 Hz, 2H, Ar-H), 7.49 (d, J=8.5 Hz, 2H, Ar-H), 7.00 (d, J=6.5 Hz, 2H, Ar-H), 6.78 (d, J=9 Hz, 2H, Ar-H), 4.98 (b, J=12 Hz, 1H, olefinic), 4.05 (t, J=13.5 Hz, 2H, -OCH_2), 3.94 (b, 1H, -COOCH), 2.56-2.63 (b, J=7 Hz, 2H, allylic methylene), 1.06-2.04 (m, 46H, 20 x CH_2, 6 x CH), 1.02 (s, 3H, -CH_3), 0.99 (d, J=5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J = 2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.69 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 161.7, 160.0, 152.2, 140.9, 132.9, 132.5, 129.8, 128.4, 128.1, 123.0, 122.3, 121.8, 114.4, 73.7, 68.5, 56.5, 56.0, 50.9, 42.8, 39.9, 39.7, 38.5, 37.3, 37.1, 36.1, 35.8, 32.2, 31.9, 31.7, 31.1, 29.5, 28.6, 28.2, 27.7, 26.4, 26.2, 25.9, 25.5, 24.7, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

2.6. 4-n-Alkyloxybenzoic acid (7a-7g) and 4-(4-n-alkyloxybenzoyloxy)benzaldehyde (8a-8g)

These intermediates were synthesized using the procedure described previously.[1]

2.7. General procedure for the Synthesis of compounds 9a-9g

A mixture of cholesteryl(1-(4-aminophenyl)-1H-1,2,3-triazole-4-carboxylate) (**4**) (0.00035 mol), 4-(4-n-alkyloxybenzoyloxy)benzaldehyde (0.00035 mol) and catalytic amount of concentrated HCl (2 drops) in chloroform was refluxed for 1 h. The reaction mixture was cooled to room temperature. The solvent was removed and repeated crystallization from ethanol to get pale yellow color solid.

9a: Yield 76 %. $C_{56}H_{72}N_4O_5$: Calc. C, 76.33; H, 8.24; N, 6.36; found C, 76.35; H, 8.23; N, 6.30. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3419, 2916, 2850 (aliphatic -CH), 1726 (ester -C=O), 1608 (imine –CH=N), 1513 (-NO2), 1270, 1229 (triazole -N=N-), 1064 (ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 8.20 (d, J=7 Hz, 2H, Ar-H), 7.88 (d, J=9 Hz, 2H, Ar-H), 7.72 (d, J=7 Hz, Ar-H), 7.55 (d, J=8 Hz, 2H, Ar-H), 7.06 (d, J=8 Hz, 2H, Ar-H), 6.98 (d, J=8 Hz, 2H, Ar-H), 4.97 (b, J=9 Hz, 1H, olefinic), 4.04 (t, J=8 Hz, 2H, -OCH_2), 3.92 (b, 1H, -COOCH), 2.55-2.60 (b, J=6 Hz, 2H, allylic methylene), 1.05-2.06 (m, 34H, 14 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.99 (d, J= -5.5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 165.7, 164.6, 160.4, 152.6, 151.9, 141.9, 133.7, 133.1, 132.9, 131.3, 130.2, 128.1, 123.5, 122.7, 121.9, 121.5, 121.3, 114.7, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 39.9, 39.8, 38.5, 37.4, 37.2, 36.1, 35.8, 32.1, 31.8, 31.8, 31.1, 29.6, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.5, 21.0, 19.3, 14.1, 12.1.

9b: Yield 78 %. $C_{57}H_{74}N_4O_5$: Calc. C, 76.47; H, 8.33; N, 6.26; found C, 76.46; H, 8.35; N, 6.21. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3417, 2916, 2850 (aliphatic -CH), 1728 (ester -C=O), 1608 (imine –CH=N), 1513 (-NO_2), 1270, 1229 (triazole -N=N-), 1064 (ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 8.21 (d, J=7 Hz, 2H, Ar-H), 7.87 (d, J=8 Hz, 2H, Ar-H), 7.72 (d, J=8 Hz, Ar-H), 7.55 (d, J=9 Hz, 2H, Ar-H), 7.06 (d, J=8.5 Hz, 2H, Ar-H), 6.97 (d, J=9 Hz, 2H, Ar-H), 4.98(b, J=9 Hz, 1H, olefinic), 4.04 (t, J=8 Hz, 2H, -OCH_2), 3.94 (b, 1H, -COOCH), 2.55-2.61 (b, J=6 Hz, 2H, allylic methylene), 1.04-2.06 (m, 36H, 15 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.99 (d, J=6 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.87 (d, J=3 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 165.7, 164.6, 160.4, 152.6, 151.8, 141.9, 133.7, 133.2, 132.9, 131.3, 130.3, 128.1, 123.5, 122.7, 121.9, 121.5, 121.3, 114.5, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 39.9, 39.8, 38.5, 37.4, 37.2,

36.1, 35.8, 32.1, 31.8, 31.8, 31.1, 29.6, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.5, 21.1, 19.3, 14.2, 12.1.

9c: Yield 80 %. $C_{58}H_{76}N_4O_5$: Calc. C, 76.62; H, 8.42; N, 6.16; found C, 76.66; H, 8.41; N, 6.14. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3417, 2915, 2852 (aliphatic –CH), 1728 (ester –C=O), 1608 (imine –CH=N), 1513 (-NO_2), 1272, 1226 (triazole -N=N-), 1064(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.51 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 8.21 (d, J=7 Hz, 2H, Ar-H), 7.87 (d, J=9 Hz, 2H, Ar-H), 7.72 (d, J=8 Hz, Ar-H), 7.55 (d, J=8 Hz, 2H, Ar-H), 7.06 (d, J=8.5 Hz, 2H, Ar-H), 6.97 (d, J=7 Hz, 2H, Ar-H), 4.98 (b, J=9 Hz, 1H, olefinic), 4.04 (t, J=8 Hz, 2H, -OCH_2), 3.93 (b, 1H, -COOCH), 2.55-2.60 (b, J=6 Hz, 2H, allylic methylene), 1.04-2.06 (m, 38H, 16 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.98 (d, J=6 Hz, 3H, CH_3), 0.93 (t, J=3 Hz, 3H, CH_3), 0.87 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 165.7, 164.6, 160.4, 152.6, 151.8, 141.9, 133.7, 133.2, 132.9, 131.3, 130.3, 128.1, 123.5, 122.6, 121.7, 121.5, 121.3, 114.6, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 40.01, 39.8, 38.5, 37.4, 37.2, 36.1, 35.8, 32.1, 31.8, 31.8, 31.2, 29.6, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.5, 21.1, 19.3, 14.2, 12.1.

9d: Yield 79 %. $C_{59}H_{78}N_4O_5$: Calc. C, 76.75; H, 8.52; N, 6.07; found C, 76.73; H, 8.58; N, 5.96. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3417, 2915, 2852 (aliphatic -CH), 1728 (ester -C=O), 1608 (imine –CH=N), 1513 (-NO_2), 1272, 1227 (triazole -N=N-), 1066(ether -C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.51 (s, 1H, -CH=N-), 8.35 (s, 1H, triazole -CH), 8.21 (d, J=7 Hz, 2H, Ar-H), 7.87 (d, J=7 Hz, 2H, Ar-H), 7.72 (d, J=7 Hz, Ar-H), 7.56 (d, J=8 Hz, 2H, Ar-H), 7.08 (d, J=6.5 Hz, 2H, Ar-H), 6.95 (d, J=7.5 Hz, 2H, Ar-H), 4.96(b, J=9 Hz, 1H, olefinic), 4.04 (t, J=8 Hz, 2H, -OCH_2), 3.97 (b, 1H, -COOCH), 2.56-2.60 (b, J=7 Hz, 2H, allylic methylene), 1.04-2.04 (m, 40H, 17 x CH_2, 6 x CH), 1.04 (s, 3H, -CH_3), 0.98 (d, J= 6 Hz, 3H, CH_3), 0.92 (t, J=3 Hz, 3H, CH_3), 0.87 (d, J=2.5 Hz, 3H, CH_3), 0.86 (d, J=2.5 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 165.7, 164.6, 160.4, 152.6, 151.8, 141.9, 133.7, 133.2, 132.9, 131.5, 130.3, 128.2, 123.5, 122.9, 121.9, 121.5, 121.5, 114.5, 73.7, 68.7, 56.5, 56.1, 50.8, 42.8, 39.9, 39.8, 38.5, 37.4, 37.2, 36.3, 35.8, 32.1, 31.8, 31.8, 31.1, 29.6, 28.6, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.5, 21.1, 19.3, 14.2, 12.1.

9e: Yield 69 %. $C_{60}H_{80}N_4O_5$: Calc. C, 76.88; H, 8.60; N, 5.98; found C, 76.93; H, 8.61; N, 6.06. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3422, 2913, 2852 (aliphatic -CH), 1728 (ester -C=O), 1608 (imine –CH=N), 1516 (-NO_2), 1272, 1229 (triazole -N=N-), 1064(ether -C-O). ^{1}H NMR ($CDCl_3$),

δ/ppm: 8.51 (s, 1H, -CH=N-), 8.36 (s, 1H, triazole -CH), 8.25 (d, J=9 Hz, 2H, Ar-H), 7.87 (d, J=7 Hz, 2H, Ar-H), 7.76 (d, J=7.5Hz, Ar-H), 7.57 (d, J=8 Hz, 2H, Ar-H), 7.05 (d, J=8 Hz, 2H, Ar-H), 6.95 (d, J=6.5 Hz, 2H, Ar-H), 4.96(b, J=8 Hz, 1H, olefinic), 4.05 (t, J=8 Hz, 2H, -OCH_2), 3.96 (b, 1H, -COOCH), 2.56-2.62 (b, J=5.5 Hz, 2H, allylic methylene), 1.05-2.04 (m, 42H, 18 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.98 (d, J=6 Hz, 3H, CH_3), 0.92 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J=4 Hz, 3H, CH_3), 0.85 (d, J=4 Hz, 3H, CH_3), 0.68 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.3, 165.7, 164.6, 160.4, 152.6, 151.8, 141.9, 133.7, 133.2, 132.9, 131.3, 130.3, 128.1, 123.5, 122.7, 121.9, 121.5, 121.3, 114.5, 73.7, 68.7, 56.5, 56.1, 50.9, 42.8, 39.9, 39.8, 38.5, 37.4, 37.2, 36.1, 35.8, 32.1, 31.8, 31.8, 31.1, 29.5, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.6, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

9f: Yield 73 %. $C_{61}H_{82}N_4O_5$: Calc. C, 77.01; H, 8.69; N, 5.89; found C, 77.03; H, 8.67; N, 5.86 FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3422, 2913, 2852 (aliphatic -CH), 1726 (ester -C=O), 1611 (imine –CH=N), 1516 (-NO_2), 1272, 1229 (triazole -N=N-), 1064(ether –C-O). ^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.33 (s, 1H, triazole -CH), 8.21 (d, J=7 Hz, 2H, Ar-H), 7.88 (d, J=8 Hz, 2H, Ar-H), 7.72 (d, J=6 Hz, Ar-H), 7.57 (d, J=8 Hz, 2H, Ar-H), 7.06 (d, J=7 Hz, 2H, Ar-H), 6.98 (d, J=8 Hz, 2H, Ar-H), 4.95 (b, J=9 Hz, 1H, olefinic), 4.04 (t, J=6 Hz, 2H, -OCH_2), 3.92 (b, 1H, -COOCH), 2.55-2.60 (b, J=6 Hz, 2H, allylic methylene), 1.05-2.06 (m, 44H, 19 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.99 (d, J= 5 Hz, 3H, CH_3), 0.91 (t, J=3 Hz, 3H, CH_3), 0.88 (d, J=4 Hz, 3H, CH_3), 0.86 (d, J=4 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.2, 165.6, 164.6, 160.4, 152.5, 151.8, 141.9, 133.7, 133.4, 132.9, 131.3, 130.1, 128.1, 123.5, 122.7, 121.9, 121.4, 121.3, 114.5, 73.7, 68.8, 56.5, 56.1, 50.9, 42.8, 39.9, 39.8, 38.5, 37.4, 37.2, 36.1, 35.8, 32.1, 31.8, 31.8, 31.2, 29.5, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.6, 23.8, 22.5, 21.1, 19.3, 14.1, 12.1.

9g: Yield 75 %. $C_{62}H_{84}N_4O_5$: Calc. C, 77.14; H, 8.77; N, 5.80; found C, 77.09; H, 8.78; N, 5.83. FT-IR (KBr pellet) υ_{max}/cm^{-1}: 3414, 2918, 2852 (aliphatic -CH), 1722 (ester -C=O), 1605 (imine –CH=N), 1514 (-NO_2), 1272, 1226 (triazole -N=N-), 1064(ether -C-O).^{1}H NMR ($CDCl_3$), δ/ppm: 8.52 (s, 1H, -CH=N-), 8.33 (s, 1H, triazole -CH), 8.21 (d, J=6 Hz, 2H, Ar-H), 7.88 (d, J=5 Hz, 2H, Ar-H), 7.72 (d, J=5.5 Hz, Ar-H), 7.57 (d, J=6 Hz, 2H, Ar-H), 7.06 (d, J=6 Hz, 2H, Ar-H), 6.98 (d, J=7 Hz, 2H, Ar-H), 4.95 (b, J=9 Hz, 1H, olefinic), 4.04 (t, J=5.5 Hz, 2H, -OCH_2), 3.92 (b, 1H, -COOCH), 2.55-2.60 (b, J=6 Hz, 2H, allylic methylene), 1.05-2.06 (m, 46H, 20 x CH_2, 6 x CH), 1.05 (s, 3H, -CH_3), 0.99 (d, J= 6 Hz, 3H, CH_3), 0.91 (t, J=4 Hz, 3H, CH_3), 0.88 (d,

J=4 Hz, 3H, CH_3), 0.86 (d, J=5.5 Hz, 3H, CH_3), 0.67 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ/ppm: 168.2, 165.6, 164.6, 160.4, 152.5, 151.8, 141.9, 133.6, 133.4, 132.9, 131.3, 130.1, 128.1, 123.5, 122.9, 121.9, 121.4, 121.3, 114.6, 73.7, 68.8, 56.5, 56.2, 50.9, 42.8, 39.9, 39.5, 38.5, 37.4, 37.2, 36.3, 35.8, 32.1, 31.8, 31.8, 31.2, 29.7, 28.5, 28.2, 27.7, 26.1, 25.9, 25.6, 24.7, 23.8, 22.4, 21.1, 19.4, 14.2, 12.1.

Reference

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