Nonsymmetrical cholesterol dimers constituting regioisomeric oxadiazole and thiadiazole cores: an investigation on structure-property correlation

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(1) Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Aluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. $^1$H and $^{13}$C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer. Polarizing optical microscope (POM) (Nikon Eclipse LV100POL) in conjunction with a controllable hot stage (Mettler Toledo FP90) was used for the characterization of mesogens. The phase transitions, associated enthalpy changes were obtained by differential scanning calorimeter (DSC) (Mettler Toledo DSC1). Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state. Atomic Force microscopy (AFM) images were obtained for the spin-coated films using Agilent 5500-STM instrument. Field Emission Scanning Electron Microscope (FESEM) images were recorded on Zeiss Sigma microscope at an accelerating voltage of 2kV, planar cells were obtained by commercially available polyimide coated cells and homeotropic cells were made by treating two cleaned glass substrates with ethyl triethoxy silane.
Reagents and Conditions (Yield): (i) n-alkyl bromide, K₂CO₃, dry DMF, 80°C, 24h (80-85%); (ii) N₂H₄·H₂O, Ethanol, 48h, reflux (75-80%); (iii) NH₂OH·HCl, Et₃N, Ethanol, 18h, reflux (78%); (iv) Benzyl bromide, K₂CO₃, dry DMF, 80°C, 24h (75%); (v) NaOH, Ethanol, 17h, reflux (90%); (vi) (a) 11, SOCl₂, 4h, reflux, (b) 15a-c, Et₃N, dry THF; (vii) POCl₃, 24h, reflux (78-85%); (viii) Lawesson’s reagent, toluene, 24h, reflux (55%); (ix) (a) 11, SOCl₂, 4h, reflux; (b) 13, Et₃N, dry pyridine, 24h, reflux (75%); (x) H₂, 10% Pd/C, dry THF, 12h (60-65%); (xi) Cholesteryl-bromoalkanoate, K₂CO₃, dry DMF, 80°C, 24h (60-82%).
(3) Experimental Section:

Procedure for the synthesis of ethyl 4-benzyloxy benzoate (12)\textsuperscript{1}:

A mixture of ethyl 4-hydroxybenzoate (9.05 mmol, 1 equiv.), anhydrous K\textsubscript{2}CO\textsubscript{3} (19.91 mmol, 2.2 equiv.), benzyl bromide (18.1 mmol, 2 equiv.) were taken in dry DMF and heated at 70°C-80°C for 36 h under argon atmosphere. After the reaction time was completed, the reaction mixture was poured into ice water and then extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and then concentrated. The crude product was purified by column chromatography on silica. Elution with hexane followed by 2-5% ethyl acetate-hexane produced the require product.

$R_f=0.4$ (5% EtOAc-hexane); oily liquid; yield: 75%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3037, 2983, 1688, 1606, 1576, 1512, 1451, 1300, 1167, 1014; $^1$H NMR (CDCl\textsubscript{3}, 600 MHz): δ 8.03 (d, 2H, $J=7.8$ Hz, H\textsubscript{Ar}), 7.44 (d, 2H, $J=7.2$ Hz, H\textsubscript{Ar}), 7.41 (t, 2H, $J=7.2$ Hz, H\textsubscript{Ar}), 7.35 (t, 1H, $J=7.2$ Hz, H\textsubscript{Ar}), 7.00 (d, 2H, $J=8.4$ Hz, H\textsubscript{Ar}), 5.11 (s, 2H, -CH\textsubscript{2}Ph), 4.37 (q, 2H, -COOCH\textsubscript{2}), 1.39 (t, 3H, CH\textsubscript{3}); $^{13}$C NMR (CDCl\textsubscript{3}, 150 MHz): 166.64, 162.54, 136.44, 131.68, 128.78, 128.30, 127.59, 123.33, 114.55, 7.019, 60.75, 14.50; HRMS (+APCI) exact mass calculated for C\textsubscript{16}H\textsubscript{17}O\textsubscript{3} (M+H\textsuperscript{+}) : 257.1178, Found: 257.1180.

Procedure for the synthesis of 4-benzyloxy benzoic acid (11)\textsuperscript{2}:

Ethyl 4-benzyloxy benzoate was dissolved in ethanol. A solution of NaOH (2 equiv.) in minimum amount of water was added to the above solution. Forth formed during the heating was dissolved by the addition of water and refluxed for 17 h. After the reaction was completed, excess of solvent was removed and the residue was added to ice water. This solution was acidified with HCl and extracted with EtOAc. The extract was dried over anhyd.Na\textsubscript{2}SO\textsubscript{4} and concentrated. The crude product was recrystallized with ethanol.

$R_f=0.2$ (30% EtOAc-hexane); orange solid; yield: 90%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3447, 3348, 2921, 2854, 1653, 1610, 1518, 1391, 1251, 827; $^1$H NMR (DMSO-d\textsubscript{6}, 600 MHz): δ 7.90 (d, 2H, $J=6$Hz, H\textsubscript{Ar}), 7.46 (d, 2H, $J=6$Hz, H\textsubscript{Ar}), 7.40 (t, 2H, $J=12$Hz, H\textsubscript{Ar}), 7.34 (t, 1H, $J=6$Hz, H\textsubscript{Ar}), 7.10 (d, 2H, $J=6$Hz, H\textsubscript{Ar}), 5.17 (s, 2H, -CH\textsubscript{2}Ph); $^{13}$C NMR (CDCl\textsubscript{3}, 150 MHz): 167.00, 161.95,
136.54, 131.37, 128.52, 128.04, 127.85, 123.18, 114.63, 69.46; HRMS (+APCI) exact mass calculated for C_{14}H_{13}O_3 (M+H^+) : 229.0865, Found: 229.0864.

**General Procedure for the synthesis of ethyl 4-n-alkoxy benzoate (16a-c)\(^1,2\):**

A mixture of ethyl 4-hydroxybenzoate (9.05 mmol, 1 equiv.), anhydrous K\(_2\)CO\(_3\) (19.91 mmol, 2.2 equiv.), \(n\)-bromoalkane (9.95 mmol, 1.1 equiv.) were taken in dry DMF and heated at \(70^\circ\text{C-80}^\circ\text{C}\) for 24h under argon atmosphere. After the reaction time was completed, the reaction mixture was poured into ice water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and then concentrated. The crude product was purified by column chromatography on silica. Elution with hexane followed by 2-5% ethyl acetate-hexane produced the require product.

**16a:** \(R_f= 0.5\) (5% EtOAc-hexane); oily liquid; yield: 80%; IR (KBr pellet): \(\nu_{\max}\) in \(\text{cm}^{-1}\) 2928, 2856, 1715, 1607, 1511, 1467, 1368, 1277, 1253,1104, 696; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.98 (d, 2H, \(J = 8.8\) Hz, H\(_{Ar}\)), 6.89 (d, 2H, \(J = 9.2\) Hz, H\(_{Ar}\)), 4.33 (q, 2H, \(J =7.6\) Hz, COOCH\(_2\)), 3.99 (t, 2H, \(J = 6.8\) Hz, OCH\(_2\)), 1.80-1.77 (m,2H, CH\(_2\)), 1.45-1.43 (m, 2H, CH\(_2\)), 1.37 (t, 3H, \(J = 7.2\) Hz, CH\(_2\)CH\(_3\)), 1.33-1.23 (m, 8H, 5×CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 166.66, 163.08, 131.69, 122.80, 114.17, 68.36, 60.78, 32.00, 29.52, 29.41, 29.30, 26.17, 22.85, 14.57, 14.29; HRMS (+APCI) exact mass calculated for C\(_{17}\)H\(_{26}\)O\(_3\) (M+H\(^+\)) : 279.1955, Found: 279.1963.

**16b:** \(R_f= 0.5\) (5% EtOAc-hexane); oily liquid; yield: 80%; IR (KBr pellet): \(\nu_{\max}\) in \(\text{cm}^{-1}\) 2928, 2857, 1714, 1607, 1511, 1468, 1368, 1312, 1253, 1105, 696; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.98 (d, 2H, \(J = 8.8\) Hz, H\(_{Ar}\)), 6.89 (d, 2H, \(J = 8.8\) Hz, H\(_{Ar}\)), 4.33 (q, 2H, \(J = 7.2\) Hz, COOCH\(_2\)), 3.99 (t, 2H, \(J = 6.4\) Hz, OCH\(_2\)), 1.82-1.69 (m,2H, CH\(_2\)), 1.47-1.43 (m, 2H, CH\(_2\)), 1.39 (t, 3H, \(J = 10\) Hz, CH\(_2\)CH\(_3\)), 1.35-1.23 (m, 10H, 5×CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 166.63, 163.06, 131.68, 122.81, 114.17, 68.35, 60.76, 32.06, 29.70, 29.56, 29.44, 29.30, 26.17, 22.86, 14.56, 14.30; HRMS (+APCI) exact mass calculated for C\(_{18}\)H\(_{28}\)O\(_3\) (M+H\(^+\)) : 293.2117, Found: 293.2116.
16c: \( R_f = 0.5 \) (5% EtOAc-hexane); oily liquid; yield: 85%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1}\): 2928, 2857, 1714, 1607, 1511, 1467, 1368, 1312, 1254, 1105, 696; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.98 (d, 2H, \( J = 8.4 \) Hz, H\(_{Ar}\)), 6.89(d, 2H, \( J = 8.8 \) Hz, H\(_{Ar}\)), 4.33 (q, 2H, \( J = 6.8 \) Hz, COOCH\(_2\)), 3.99 (t, 2H, \( J = 6.8 \) Hz, OCH\(_2\)), 1.82-1.75 (m,2H, CH\(_2\)), 1.45-1.41 (m, 2H, CH\(_2\)), 1.37 (t, 3H, \( J = 7.2 \) Hz, CH\(_2\)CH\(_3\)), 1.31-1.27(m, 12H, 6\( \times \)CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR(CDCl\(_3\), 100 MHz): 166.65, 163.05, 131.68, 122.78, 114.16, 68.35, 60.77, 32.07, 29.73, 29.55, 29.29, 26.16, 22.87, 14.56, 14.31; HRMS (+APCI) exact mass calculated for C\(_{19}\)H\(_{30}\)O\(_3\) (M+H\(^{+}\)) : 307.2273, Found: 307.2274.

General Procedure for the synthesis of ethyl 4-\( n \)-alkoxy benzhydrazide (15a-c)\(^{1,2}\):

A mixture of ethyl 4-\( n \)-alkoxy benzoate (9 mmol, 1equiv.), excess hydrazine hydrate (20 equiv.) in ethanol was refluxed for 48 h. Excess solvent was removed and water was added to it. Resulting precipitate was collected by filtration, washed with excess water, dried under vacuum, and recrystallization from ethanol gave pure white solid product.

15a: \( R_f = 0.25 \) (40% EtOAc-hexanes); white solid; yield: 75%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1}\) 3314, 2925, 1657, 1539, 1304, 1253, 1183, 1066, 839, 767; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.70 (d, 2H, \( J = 5.6 \) Hz, H\(_{Ar}\)), 7.55 (br s, 1H,CONH), 6.90 (d, 2H, \( J = 6 \) Hz, H\(_{Ar}\)), 3.98 (t, 2H, \( J = 4.4 \) Hz, OCH\(_2\)), 3.32 (br s, 2H, NH\(_2\)), 1.76-1.80 (m, 2H, CH\(_2\)),1.42-1.47 (m, 2H, CH\(_2\)),1.25-1.35 (m, 8H, 4\( \times \)CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 168.54, 162.20, 128.85, 124.66, 114.49, 68.33, 131.95, 29.47, 29.37, 29.25, 26.13, 22.80, 14.26; HRMS (+APCI) exact mass calculated for C\(_{19}\)H\(_{24}\)N\(_2\)O\(_2\)K (M+K\(^{+}\)) : 305.1456, Found: 305.2238.

15b: \( R_f = 0.25 \) (40% EtOAc-hexanes); white solid; yield: 78%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1}\) 3321, 2916, 1647, 1569, 1304, 1251, 1184, 1026, 834, 756; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 7.70 (d, 2H, \( J = 4.8 \) Hz, H\(_{Ar}\)), 7.25 (br s, 1H,CONH), 6.92 (d, 2H, \( J = 4.8 \) Hz, H\(_{Ar}\)), 4.07 (br s, 2H, NH\(_2\)), 3.99 (t, 2H, \( J = 4.4 \) Hz, OCH\(_2\)), 1.78-1.80 (m, 2H, CH\(_2\)),1.44-1.46 (m, 2H, CH\(_2\)), 1.27-1.36 (m, 10H, 5\( \times \)CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): 168.57, 162.26, 128.85, 124.72, 114.54, 68.38, 32.03, 29.69, 29.54, 29.42, 29.28,26.15, 22.84, 14.28; HRMS (+APCI) exact mass calculated for C\(_{16}\)H\(_{27}\)N\(_2\)O\(_2\) (M+H\(^{+}\)) : 279.2073, Found: 279.2073.
15c: $R_f= 0.25$ (40% EtOAc-hexane); white solid; yield: 80%; IR (KBr pellet): $v_{\text{max}}$ in cm$^{-1}$ 3322, 2916, 1646, 1569, 1304, 1251, 1184, 1016, 834, 755; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.70 (d, 2H, $J = 6$ Hz, H$_{Ar}$), 7.31 (br s, 1H, CONH), 6.92 (d, 2H, $J = 6$ Hz, H$_{Ar}$), 4.07 (br s, 2H, NH$_2$), 3.99 (t, 2H, $J = 4.4$ Hz, OCH$_2$), 1.76-1.80 (m, 2H, CH$_2$), 1.42-1.46 (m, 2H, CH$_2$), 1.27-1.36 (m, 12H, 6×CH$_2$), 0.88 (t, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 100 MHz): 168.64, 162.35, 128.80, 124.77, 114.67, 68.45, 32.10, 29.76, 29.57, 29.52, 29.33, 26.19, 22.89, 14.32; HRMS (+APCI) exact mass calculated for C$_{17}$H$_{29}$N$_2$O$_2$ (M+H$^+$): 293.2229, Found: 293.2229.

General Procedure for the synthesis of 2-(4-(benzyloxy) phenyl)-5-(4-(alkoxy) phenyl)-1,3, 4-oxadiazole (5a-c):

4-benzyloxy benzoic acid (2.5mmol) in 6 ml of thionyl chloride and catalytic amount of DMF was refluxed for 4 h. The excess of thionyl chloride was removed by distillation and then the crude product was dried in vacuo and used for the next reaction without further purification and characterization.

A solution of 4-benzyloxy benzoic acid chloride (2.2 mmol, 1equiv.) in THF was added dropwise into a solution of ethyl 4-n-alkoxy benzohydrazide (15a-c) (2.31 mmol, 1.05equiv.) and triethylamine (2.2mmol, 1equiv.) in THF. The reaction mixture was refluxed for 24 h. After cooling to room temperature, THF was evaporated in rotavapor and the residue was extracted with ethyl acetate and concentrated. The resulting crude product (8a-c) was directly used for next reaction. The crude product 8a-c (0.3mmol, 1equiv.) was dissolved in POCl$_3$ and refluxed for about 24 h. The residue was slowly added to ice water and extracted with DCM. The combine extract was washed with brine, dried over anhydrous Na$_2$SO$_4$ and then concentrated. Then, the crude product was further purified through column chromatography on neutral alumina. Elution with 60-70% DCM-hexane produced the require product.

5a: $R_f= 0.45$ (80% DCM-hexane); white solid; yield: 85%; IR (KBr pellet): $v_{\text{max}}$ in cm$^{-1}$ 2921, 2851, 1607, 1516, 1468, 1306, 1255, 1174, 1037, 831; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.06 (d, 2H, $J = 8.4$ Hz, H$_{Ar}$), 8.04 (d, 2H, $J = 8.4$ Hz, H$_{Ar}$), 7.46 (d, 2H, $J = 7.2$ Hz, H$_{Ar}$), 7.41 (t, 2H, $J = 7.8$Hz, H$_{Ar}$), 7.35 (t, 1H, $J = 7.2$Hz, H$_{Ar}$), 7.10 (d, 2H, $J = 9$ Hz, H$_{Ar}$), 7.01 (d, 2H, $J = 9$Hz, H$_{Ar}$), 5.15 (s, 2H, OCH$_2$Ph), 4.03 (t, 2H, $J = 6.6$ Hz, OCH$_2$), 1.79-1.84 (m, 2H, CH$_2$), 1.45-1.49 (m,
2H, CH₂), 1.27-1.38 (m, 8H, 4×CH₂), 0.89 (t, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 164.40, 164.21, 162.04, 161.52, 136.42, 128.91, 128.80, 128.76, 128.46, 127.73, 117.08, 116.50, 115.53, 115.14, 70.37, 68.48, 32.01, 29.55, 29.44, 29.34, 26.21, 22.87, 14.32; HRMS (+APCI) exact mass calculated for C₂₉H₃₃N₂O₃ (M+H⁺): 457.2491, Found: 457.2045.

5b: Rᵣ = 0.45 (80% DCM-hexane); white solid; yield: 83%; IR (KBr pellet): νmax in cm⁻¹ 2920, 2851, 1607, 1516, 1469, 1306, 1256, 1173, 1037, 831; ¹H NMR (CDCl₃, 600 MHz): δ 8.06 (d, 2H, J = 9 Hz, HAr), 8.04 (d, 2H, J = 9Hz, HAr), 7.45 (d, 2H, J = 7.2 Hz, HAr), 7.41 (t, 2H, J = 7.2Hz, HAr), 7.35 (t, 1H, J = 7.2 Hz, HAr), 7.10 (d, 2H, J = 9 Hz, HAr), 7.01 (d, 2H, J = 9 Hz, HAr), 5.15 (s, 2H, OCH₂Ph), 4.03 (t, 2H, J = 6 Hz, OCH₂), 1.79-1.84 (m, 2H, CH₂), 1.45-1.50 (m, 2H, CH₂), 1.29-1.37 (m, 8H, 4×CH₂), 0.88(t, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 164.40, 164.21, 162.04, 161.53, 136.42, 128.92, 128.80, 128.76, 128.46, 127.72, 117.06, 116.48, 115.53, 115.14, 70.37, 68.47, 32.07, 29.73, 29.58, 29.46, 29.33, 26.20, 22.88, 14.33; HRMS (+APCI) exact mass calculated for C₃₀H₃₅N₂O₃ (M+H⁺): 471.2648, Found: 471.2378.

5c: Rᵣ = 0.45 (80% DCM-hexane); white solid; yield: 78%; IR (KBr pellet): νmax in cm⁻¹ 2920, 2851, 1607, 1516, 1469, 1444, 1256, 1173, 1037, 831; ¹H NMR (CDCl₃, 600 MHz): δ 8.06 (d, 2H, J = 9 Hz, HAr), 8.04 (d, 2H, J = 9Hz, HAr), 7.45 (d, 2H, J = 7.2 Hz, HAr), 7.41 (t, 2H, J = 7.2Hz, HAr), 7.35 (t, 1H, J = 7.2 Hz, HAr), 7.10 (d, 2H, J = 8.4 Hz, HAr), 7.01 (d, 2H, J = 8.4Hz, HAr), 5.15 (s, 2H, OCH₂Ph), 4.03 (t, 2H, J = 6 Hz, OCH₂), 1.80-1.84 (m, 2H, CH₂), 1.45-1.50 (m, 2H, CH₂), 1.28-1.37 (m, 12H, 6×CH₂), 0.88 (t, 3H, CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 164.42, 164.22, 162.08, 161.57, 136.46, 128.93, 128.81, 128.77, 128.46, 127.73, 117.12, 116.53, 115.57, 115.18, 70.41, 68.50, 32.11, 29.77, 29.59, 29.53, 29.36, 26.22, 22.89, 14.32; HRMS (+APCI) exact mass calculated for C₃₁H₃₇N₂O₃ (M+H⁺): 485.2804, Found: 485.2525.

General Procedure for the synthesis of 4-(5-(4-(alkoxy)phenyl)-1,3,4-oxadiazol-2-yl) phenol(4a-e)⁵:

2-(4-(benzylxy) phenyl)-5-(4-(alkoxy) phenyl)-1,3,4-oxadiazole (5a-c) was dissolved in dry THF and degassed with nitrogen for 10-15 minutes. Then, 10 mol% of Pd/C was added to the above reaction mixture. The reaction was carried out under H₂ gas overnight. After the reaction
was completed, mixture was filtered in celite bed to remove Pd/C and washed with ethyl acetate. The filtrate was concentrated and then the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 40% EtOAc-hexanes produced the require product.

4a: \( R_f = 0.25 \) (50% EtOAc-hexane); white solid; yield: 65%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1} \) 3104, 2922, 2851, 1612, 1497, 1391, 1290, 1262, 1174, 844; \(^1\)H NMR (CDCl\(_3\), 600 MHz): \( \delta \) 8.03 (d, 2H, \( J = 9.6 \) Hz, H\(_{\text{Ar}}\)), 8.00 (d, 2H, \( J = 9.6 \) Hz, H\(_{\text{Ar}}\)), 7.07 (d, 2H, \( J = 8.8 \) Hz, H\(_{\text{Ar}}\)), 7.01 (d, 2H, \( J = 10 \) Hz, H\(_{\text{Ar}}\)), 4.02 (t, 2H, OCH\(_2\)), 1.78-1.83 (m, 4H, 2\( \times \)CH\(_2\)), 1.45-1.48 (m, 2H, CH\(_2\)), 1.25-1.33 (m, 6H, 3\( \times \)CH\(_2\)), 0.89 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz): \( \delta \) 164.64, 164.37, 162.27, 160.37, 129.10, 128.84, 116.66, 116.00, 115.49, 115.25, 68.53, 32.10, 29.76, 29.58, 29.52, 29.33, 26.19, 22.88, 14.32; HRMS (+APCI) exact mass calculated for C\(_{22}\)H\(_{27}\)N\(_2\)O\(_3\) (M+H\(^+\)): 367.2022, Found: 367.1603.

4b: \( R_f = 0.25 \) (50% EtOAc-hexane); white solid; yield: 60%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1} \) 3104, 2922, 2851, 1899, 1612, 1497, 1391, 1262, 1174, 844; \(^1\)H NMR (CDCl\(_3\), 600 MHz): \( \delta \) 8.04 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 8.01 (d, 2H, \( J = 9 \) Hz, H\(_{\text{Ar}}\)), 7.32 (s, 1H, -OH), 7.05 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 7.01 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 4.03 (t, 2H, \( J = 6.6 \) Hz, OCH\(_2\)), 1.79-1.84 (m, 2H, CH\(_2\)), 1.26-1.37 (m, 10H, 5\( \times \)CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz): \( \delta \) 164.46, 164.40, 162.18, 159.66, 129.09, 128.83, 116.48, 116.22, 116.19, 115.22, 68.51, 32.09, 29.74, 29.59, 29.47, 29.33, 26.21, 22.88, 14.34; HRMS (+APCI) exact mass calculated for C\(_{23}\)H\(_{29}\)N\(_2\)O\(_3\) (M+H\(^+\)): 381.2178, Found: 381.2015.

4c: \( R_f = 0.25 \) (50% EtOAc-hexane); white solid; yield: 63%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1} \) 3104, 2922, 2851, 1612, 1497, 1391, 1262, 1174, 1019, 844; \(^1\)H NMR (CDCl\(_3\), 600 MHz): \( \delta \) 8.02 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 7.98 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 7.08 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 7.00 (d, 2H, \( J = 8.4 \) Hz, H\(_{\text{Ar}}\)), 4.01 (t, 2H, \( J = 6 \) Hz, OCH\(_2\)), 1.78-1.83 (m, 2H, CH\(_2\)), 1.44-1.47 (m, 2H, CH\(_2\)), 1.28-1.36 (m, 12H, 6\( \times \)CH\(_2\)), 0.88 (t, 3H, CH\(_3\)); \(^{13}\)C NMR (CDCl\(_3\), 150 MHz): \( \delta \) 164.64, 164.37, 162.27, 160.37, 129.10, 128.84, 116.66, 116.00, 115.49, 115.25, 68.53, 32.10, 29.76, 29.58, 29.52, 29.33, 26.19, 22.88, 14.32; HRMS (+APCI) exact mass calculated for C\(_{24}\)H\(_{31}\)N\(_2\)O\(_3\) (M+H\(^+\)): 395.2335, Found: 395.2327.
Procedure for the synthesis of 1-n/R:

A mixture of appropriate compound (3a-c) (1.1 mmol, 1.1 equiv.), anhydrous K$_2$CO$_3$ (2.2 mmol, 2.2 equiv.), cholesteryl ω-bromoalkanoate (1 mmol, 1 equiv.) were taken in dry DMF and heated under argon atmosphere at 70°C-80°C for 24 h. After the reaction time was completed, the reaction mixture was poured into ice water and then extracted with DCM. The combine extract was washed with brine, dried over anhydrous Na$_2$SO$_4$ and then concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with 40-50% DCM-hexane produced the require product.

1-3/8: $R_f$ = 0.45 (30% DCM-hexane); white solid; yield: 75%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3558, 3377, 2929, 1637, 1499, 1367, 1257, 1173, 1023, 836; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.04 (d, 4H, J = 12 Hz, H$_{Ar}$), 7.01 (d, 4H, J = 6 Hz, H$_{Ar}$), 5.37 (d, 1H, J = 6 Hz, 1 × olefinic H), 4.61 – 4.65 (m, 1H, 1 × CHOOCO), 4.09 (t, 2H, J = 6 Hz, 1 × OCH$_2$), 4.03 (t, 2H, J = 6 Hz, 1 × OCH$_2$), 2.52 (t, 2H, J = 6 Hz, 1 × CH$_2$), 2.32 (d, 2H, 1 × CH$_2$), 2.14 (t, 2H, J = 6 Hz, 1 × CH$_2$) 1.28 – 2.01 (m, 38H, 16 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.87 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.67 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 172.75, 164.46, 164.25, 162.05, 161.69, 139.80, 128.77, 122.95, 117.18, 116.57, 115.16, 74.39, 68.49, 67.24, 56.90, 56.35, 50.23, 45.52, 39.94, 39.73, 38.36, 37.19, 36.40, 36.00, 32.12, 32.02, 31.24, 29.92, 29.56, 29.44, 28.44, 28.23, 28.03, 26.22, 24.79, 24.50, 24.04, 23.04, 22.87, 22.77, 21.24, 19.52, 18.92, 14.32, 12.07; MALDI-TOF exact mass calculated for C$_{53}$H$_{76}$N$_2$O$_5$(M$^+$): 820.5754, Found: 820.5347.

1-4/8: $R_f$ = 0.45 (30% DCM-hexane); white solid; yield: 67%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3558, 3377, 2929, 1637, 1499, 1367, 1257, 1173, 1023, 836; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.04 (d, 4H, J = 12 Hz, H$_{Ar}$), 7.01 (d, 2H, J = 6 Hz, H$_{Ar}$), 7.00 (d, 2H, J = 6 Hz, H$_{Ar}$), 5.37 (d, 1H, J = 6 Hz, 1 × olefinic H), 4.59 – 4.65 (m, 1H, 1 × CHOOCO), 4.09 (t, 2H, J = 6 Hz, 1 × OCH$_2$), 4.03 (t, 2H, J = 6 Hz, 1 × OCH$_2$), 2.38 (t, 2H, J = 6 Hz, 1 × CH$_2$), 2.31 (d, 2H, 1 × CH$_2$), 1.02 – 2.00 (m, 42H, 18 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.89 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.87 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6 Hz, 1 × CH$_3$), 0.66 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 172.98, 164.38, 164.29, 162.06, 161.80, 139.85, 128.78, 122.90, 116.80, 116.60, 115.18, 74.20, 68.51, 67.88, 56.91, 56.37, 50.26, 42.53, 39.95, 39.74, 38.38,
37.23, 36.81, 36.41, 36.01, 34.47, 32.12, 32.02, 29.55, 29.43, 29.36, 28.73, 28.44, 28.23, 28.06, 26.23, 24.49, 24.06, 23.03, 22.87, 22.77, 21.89, 21.25, 19.53, 18.93, 14.30, 12.06; MALDI-TOF exact mass calculated for $C_{54}H_{78}N_2O_5(M^+)$: 834.5911, Found: 834.7130.

1-5/8: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 79%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3558, 3377, 2929, 1637, 1499, 1367, 1257, 1173, 1023, 836; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.04 (d, 4H, $J = 12$Hz, H$_{Ar}$), 7.02 (d, 2H, $J = 6$Hz, H$_{Ar}$), 7.00 (d, 2H, $J = 6$Hz, H$_{Ar}$), 5.37 (d, 1H, $J = 6$Hz, 1 × olefinic H), 4.59 – 4.65 (m, 1H, 1 × CHOCO), 4.06 (t, 2H, $J = 6$Hz, 1 × OCH$_2$), 4.03 (t, 2H, $J = 6$Hz, 1 × OCH$_2$), 2.38 (t, 2H, 1 × CH$_2$), 2.31 (d, 2H, 1 × CH$_2$), 1.03 – 2.01 (m, 44H, 19 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, $J = 6$Hz, 1 × CH$_3$), 0.87 (d, 3H, $J = 6$Hz, 1 × CH$_3$), 0.86 (d, 3H, $J = 6$Hz, 1 × CH$_3$), 0.66 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 172.98, 164.33, 164.26, 162.01, 161.75, 139.79, 128.75, 122.89, 116.73, 116.53, 115.13, 74.17, 68.47, 67.83, 56.87, 56.32, 50.20, 42.50, 39.72, 37.18, 36.79, 36.38, 36.00, 32.10, 32.04, 32.02, 29.55, 29.44, 29.35, 28.71, 28.44, 28.23, 28.02, 26.22, 24.04, 23.04, 22.87, 21.88, 19.53, 14.33, 12.06; MALDI-TOF exact mass calculated for $C_{55}H_{80}N_2O_5(M^+)$: 848.6067, Found: 848.5260.

1-7/8: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 73%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3558, 3377, 2929, 1637, 1499, 1367, 1257, 1173, 1023, 836; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.04 (d, 4H, $J = 12$Hz, H$_{Ar}$), 7.00 (d, 4H, $J = 12$Hz, H$_{Ar}$), 5.37 (d, 1H, $J = 6$Hz, 1 × olefinic H), 4.57 – 4.62 (m, 1H, 1 × CHOCO), 4.01 – 4.04 (m, 4H, 2 × OCH$_2$), 2.26 – 2.31 (m, 4H, 2 × CH$_2$), 1.03 – 2.01 (m, 44H, 19 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, $J = 6$Hz, 1 × CH$_3$), 0.87 (d, 3H, $J = 6$Hz, 1 × CH$_3$), 0.85 (s, 3H, 1 × CH$_3$), 0.66 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 173.45, 164.35, 164.26, 161.75, 139.79, 128.75, 122.89, 116.73, 116.53, 115.13, 74.17, 68.47, 67.83, 56.87, 56.32, 50.20, 42.50, 39.72, 37.18, 36.79, 36.38, 36.00, 32.10, 32.04, 32.02, 29.55, 29.44, 29.35, 28.71, 28.44, 28.23, 28.02, 26.22, 24.04, 23.04, 22.87, 21.88, 19.53, 14.32, 12.06; MALDI-TOF exact mass calculated for $C_{55}H_{80}N_2O_5(M^+)$: 848.6067, Found: 848.5260.

1-3/9: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3377, 2927, 2079, 1741, 1611, 1502, 1470, 1420, 1172, 837; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.04 (d, 4H, $J = 12$Hz, H$_{Ar}$), 7.01 (d, 4H, $J = 6$Hz, H$_{Ar}$), 5.37 (s, 1H, 1 × olefinic H), 4.63 – 4.65 (m, 1H, 1
× CHOCO), 4.09 (t, 2H, J = 6Hz, 1 × OCH₂), 4.03 (t, 2H, J = 6Hz, 1 × OCH₂), 2.52 (t, 2H, J = 6Hz, 1 × CH₂), 2.32 (t, 2H, J = 6Hz, 1 × CH₂), 2.15 (t, 2H, J = 6Hz, 1 × CH₂), 1.04 – 2.01 (m, 40H, 17 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, 3H, J = 6Hz, 1 × CH₃), 0.89 (s, 3H, 1 × CH₃), 0.86 (s, 3H, 1 × CH₃), 0.85 (d, 3H, J = 6Hz, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 172.69, 164.60, 164.27, 162.07, 161.70, 139.81, 128.80, 122.96, 116.90, 116.56, 115.17, 74.40, 68.50, 67.25, 56.90, 56.36, 50.24, 42.53, 39.94, 39.74, 38.36, 37.19, 36.82, 36.40, 36.00, 32.08, 31.25, 29.91, 29.73, 29.59, 29.47, 29.35, 28.43, 28.23, 28.03, 26.22, 24.79, 24.49, 24.04, 23.02, 22.88, 22.77, 21.24, 19.52, 18.93, 14.32, 12.07; MALDI-TOF exact mass calculated for C₅₄H₇₈N₂O₅(M⁺): 834.5911, Found: 834.7130.

1-4/9: R₁ = 0.45 (30% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): νmax in cm⁻¹: 3377, 2927, 2079, 1741, 1611, 1502, 1470, 1420, 1172, 837; ¹H NMR (CDCl₃, 600 MHz): δ 8.04 (d, 4H, J = 12Hz, H Ar), 7.01 (d, 2H, J = 6Hz, H Ar), 7.00 (d, 2H, J = 6Hz, H Ar), 5.37 (d, 1H, J = 6Hz, 1 × olefinic H), 4.59 – 4.65 (m, 1H, 1 × CHOCO), 4.06 (t, 2H, J = 6Hz, 1 × OCH₂), 4.03 (t, 2H, J = 6Hz, 1 × OCH₂), 2.38 (t, 2H, J = 6Hz, 1 × CH₂), 2.31 (t, 2H, J = 6Hz, 1 × CH₂), 1.02 – 2.01 (m, 44H, 19 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, 3H, J = 6Hz, 1 × CH₃), 0.88 (d, 3H, J = 6Hz, 1 × CH₃), 0.87 (d, 3H, J = 6Hz, 1 × CH₃), 0.86 (d, 3H, J = 6Hz, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 172.99, 164.37, 164.29, 162.06, 161.79, 139.83, 128.78, 122.91, 116.78, 116.58, 115.17, 74.19, 68.50, 67.87, 56.90, 56.35, 50.24, 42.52, 39.94, 39.74, 38.37, 37.20, 36.80, 36.40, 36.00, 34.46, 32.11, 32.07, 29.73, 28.43, 28.23, 28.03, 26.22, 24.48, 24.04, 23.02, 22.87, 21.89, 21.24, 19.52, 18.92, 14.32, 12.06; MALDI-TOF exact mass calculated for C₅₃H₇₈N₂O₅(M⁺): 849.6145, Found: 849.7173.

1-5/9: R₁ = 0.45 (30% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): νmax in cm⁻¹: 3377, 2927, 2079, 1741, 1611, 1502, 1470, 1420, 1172, 837; ¹H NMR (CDCl₃, 600 MHz): δ 8.04 (d, 4H, J = 12Hz, H Ar), 7.01 (d, 4H, J = 12Hz, H Ar), 5.37 (d, 1H, J = 6Hz, 1 × olefinic H), 4.59 – 4.65 (m, 1H, 1 × CHOCO), 4.06 (t, 2H, J = 6Hz, 1 × OCH₂), 4.03 (t, 2H, J = 6Hz, 1 × OCH₂), 2.38 (t, 2H, J = 6Hz, 1 × CH₂), 2.31 (t, 2H, J = 6Hz, 1 × CH₂), 1.03 – 2.00 (m, 46H, 20 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, 3H, J = 6Hz, 1 × CH₃), 0.88 (d, 3H, J = 6Hz, 1 × CH₃), 0.87 (d, 3H, J = 6Hz, 1 × CH₃), 0.86 (d, 3H, J = 6Hz, 1 × CH₃), 0.66 (s, 3H, 1 × CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 172.99, 164.37, 164.28, 162.06, 161.79, 139.82, 128.77, 122.91, 116.77, 116.57, 115.36, 74.19, 68.49, 67.86, 56.89, 56.34, 50.23, 42.52, 39.93, 39.73, 38.36, 37.19, S12
36.80, 36.39, 36.00, 34.45, 32.10, 29.90, 29.73, 29.59, 29.47, 29.36, 28.72, 28.43, 28.23, 28.03, 26.21, 24.48, 24.04, 23.03, 22.88, 22.77, 21.88, 21.24, 19.52, 18.92; MALDI-TOF exact mass calculated for C$_{56}$H$_{83}$N$_2$O$_5$(M+H$^+$): 863.6302, Found: 863.4229.

1-7/9: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3377, 2927, 2079, 1741, 1611, 1502, 1470, 1420, 1172, 837; $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.04 (d, 4H, J = 12Hz, H$_A$), 7.01 (d, 4H, J = 6Hz, H$_A$), 5.37 (s, 1H, 1 × olefinic H), 4.63 – 4.65 (m, 1H, 1 × CHOCO), 4.09 (t, 2H, J = 6Hz, 1 × OCH$_2$), 4.03 (t, 2H, J = 6Hz, 1 × OCH$_2$), 2.52 (t, 2H, J = 6Hz, 1 × CH$_2$), 2.32 (t, 2H, J = 6Hz, 1 × CH$_2$), 2.15 (t, 2H, J = 6Hz, 1 × CH$_2$), 1.04 – 2.01 (m, 48H, 21 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.89 (s, 3H, 1 × CH$_3$), 0.86 (s, 3H, 1 × CH$_3$), 0.85 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.67 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 173.37, 164.55, 164.24, 161.98, 139.82, 128.78, 122.77, 116.51, 115.08, 73.91, 68.41, 68.28, 63.06, 56.83, 56.29, 50.17, 42.45, 39.88, 39.68, 38.32, 37.15, 36.74, 36.34, 35.95, 34.78, 32.86, 32.06, 32.00, 29.87, 29.69, 29.56, 29.43, 29.21, 29.14, 28.39, 28.17, 27.97, 26.17, 25.98, 25.74, 25.09, 24.44, 24.01, 22.99, 22.84, 22.74, 21.18, 19.47, 18.87, 14.29, 12.00; MALDI-TOF exact mass calculated for C$_{58}$H$_{87}$N$_2$O$_5$(M+H$^+$): 891.6615, Found: 891.7270.

1-3/10: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 82%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3640, 3203, 2929, 2070, 1637, 1499, 1367, 1173, 836, 741; $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.02 (d, 4H, J = 6Hz, H$_A$), 6.99 (d, 4H, J = 6Hz, H$_A$), 5.35 (s, 1H, 1 × olefinic H), 4.61 – 4.63 (m, 1H, 1 × CHOCO), 4.07 (t, 2H, J = 6Hz, 1 × OCH$_2$), 4.00 (t, 2H, J = 6Hz, 1 × OCH$_2$), 2.50 (t, 2H, J = 6Hz, 1 × CH$_2$), 2.31 (d, 2H, J = 6Hz, 1 × CH$_2$), 2.11 – 2.15 (m, 2H, 1 × CH$_2$), 1.06 – 2.00 (m, 42, 18 × CH$_2$, 6 × CH), 0.99 (s, 3H, 1 × CH$_3$), 0.90 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.88 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.84 (s, 3H, 1 × CH$_3$), 0.66 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 172.60, 164.30, 162.68, 161.99, 161.64, 139.74, 128.71, 122.88, 116.83, 116.49, 115.10, 74.33, 68.42, 67.79, 56.84, 56.30, 42.46, 39.98, 39.68, 38.31, 37.14, 36.75, 36.62, 36.35, 35.96, 32.06, 32.01, 31.58, 31.18, 29.87, 29.73, 29.55, 29.48, 29.31, 29.09, 28.39, 28.17, 27.98, 26.17, 24.74, 24.44, 24.00, 22.98, 22.85, 22.73, 21.19, 19.46, 18.88, 14.29, 12.01; MALDI-TOF exact mass calculated for C$_{55}$H$_{87}$N$_2$O$_5$(M+H$^+$): 849.6145, Found: 849.7173.

1-4/10: $R_f = 0.45$ (30% DCM-hexane); white solid; yield: 78%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3444, 2938, 1742, 1611, 1503, 1420, 1304, 1220, 1172, 1022; $^1$H NMR (CDCl$_3$, 600 MHz): δ
8.04 (d, 4H, J = 6Hz, H_{Ar}), 7.00 (d, 4H, J = 6Hz, H_{Ar}), 5.36 (s, 1H, 1 × olefinic H), 4.61 – 4.62 (m, 1H, 1 × CHOCO), 4.01-4.05 (m, 4H, 2 × OCH2), 2.38 (t, 2H, J = 6Hz, 1 × CH2), 2.31 (d, 2H, J = 6Hz, 1 × CH2), 1.03 – 2.00 (m, 46H, 20 × CH2, 6 × CH), 1.01 (s, 3H, 1 × CH3), 0.91 (d, 3H, J = 6Hz, 1 × CH3), 0.88 (s, 3H, 1 × CH3), 0.87 (d, 3H, J = 6Hz, 1 × CH3), 0.86 (s, 3H, 1 × CH3), 0.66 (s, 3H, 1 × CH3); ^{13}C NMR (CDCl3, 150 MHz): δ 172.97, 164.35, 164.28, 162.05, 161.79, 141.00, 139.82, 128.76, 122.90, 121.90, 116.78, 116.58, 115.36, 74.18, 68.49, 67.85, 56.89, 56.34, 50.32, 45.52, 39.93, 39.73, 38.36, 37.19, 36.80, 36.39, 36.00, 34.45, 32.11, 32.06, 29.76, 29.58, 29.52, 29.35, 28.72, 28.43, 28.22, 28.02, 26.21, 24.48, 24.04, 23.03, 22.89, 22.77, 21.88, 21.24, 19.52, 18.92, 14.32, 12.06; MALDI-TOF exact mass calculated for C_{56}H_{83}N_{2}O_{5}(M^+): 863.6302, Found: 863.4229.

1-5/10: \( R_f = 0.45 \) (30% DCM-hexane); white solid; yield: 72%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1}\) 3640, 3203, 2929, 2970, 1637, 1499, 1367, 1173, 836, 741; \(^{1}\)H NMR (CDCl3, 600 MHz): δ 8.04 (d, 4H, J = 6Hz, H_{Ar}), 7.01 (d, 4H, J = 6Hz, H_{Ar}), 5.37 (d, 1H, J = 6Hz 1 × olefinic H), 4.59 – 4.65 (m, 1H, 1 × CHOCO), 4.06 (t, 2H, J = 6Hz, 1 × OCH2), 4.03 (t, 2H, J = 6Hz, 1 × OCH2), 2.32 (t, 2H, J = 6Hz, 1 × CH2), 2.31 (t, 2H, J = 6Hz, 1 × CH2), 2.31 (d, 2H, J = 6Hz, 1 × CH2), 1.09 – 2.01 (m, 48H, 21 × CH2, 6 × CH), 1.01 (s, 3H, 1 × CH3), 0.91 (d, 3H, J = 6Hz, 1 × CH3), 0.89 (d, 3H, J = 6Hz, 1 × CH3), 0.87 (d, 3H, 1 × CH3), 0.86 (d, 3H, J = 6Hz, 1 × CH3), 0.66 (s, 3H, 1 × CH3); \(^{13}\)C NMR (CDCl3, 150 MHz): δ 172.98, 164.37, 164.28, 162.06, 161.79, 139.89, 128.77, 122.91, 116.78, 116.58, 115.16, 74.18, 68.50, 67.86, 56.90, 56.35, 50.24, 42.52, 39.94, 39.74, 38.37, 37.20, 36.80, 36.40, 36.00, 34.46, 32.11, 32.07, 29.77, 29.59, 29.53, 29.35, 28.72, 28.43, 28.23, 26.22, 24.48, 24.04, 23.03, 22.89, 22.77, 21.89, 21.24, 19.52, 18.92, 14.33, 12.07; MALDI-TOF exact mass calculated for C_{57}H_{84}N_{2}O_{5}(M^+): 876.6380, Found: 876.5950.

1-7/10: \( R_f = 0.45 \) (30% DCM-hexane); white solid; yield: 75%; IR (KBr pellet): \( \nu_{\text{max}} \) in cm\(^{-1}\) 3444, 2938, 1742, 1611, 1503, 1420, 1304, 1220, 1172, 1022; \(^{1}\)H NMR (CDCl3, 600 MHz): δ 8.01 (d, 4H, J = 6Hz, H_{Ar}), 6.98 (d, 4H, J = 6Hz, H_{Ar}), 5.34 (s, 1H, 1 × olefinic H), 4.59 – 4.60 (m, 1H, 1 × CHOCO), 3.99 (m, 4H, 2 × OCH2), 2.25 – 2.30 (m, 4H, 2 × CH2), 1.02 – 2.02 (m, 52H, 23 × CH2, 6 × CH), 0.99 (s, 3H, 1 × CH3), 0.89 (d, 3H, J = 6Hz, 1 × CH3), 0.87 (s, 3H, 1 × CH3), 0.86 (d, 3H, J = 6Hz, 1 × CH3), 0.85 (s, 3H, 1 × CH3), 0.65 (s, 3H, 1 × CH3); \(^{13}\)C NMR (CDCl3, 150 MHz): δ 173.31, 164.21, 162.61, 161.96, 161.90, 139.81, 128.65, 122.75, 116.53, 116.50, 115.06, 73.87, 68.39, 68.27, 56.81, 56.28, 50.16, 42.44, 39.86, 39.86, 39.67, 38.32, 38.32,
37.13, 36.73, 36.33, 35.94, 34.76, 32.04, 31.99, 29.86, 29.72, 29.54, 29.48, 29.30, 29.12, 28.37, 28.15, 27.96, 26.15, 25.96, 25.07, 24.42, 24.00, 22.97, 22.83, 22.72, 21.17, 19.45, 18.86, 14.27, 11.98; MALDI-TOF exact mass calculated for C$_{59}$H$_{88}$N$_2$O$_5$(M$^+$): 904.6693, Found:904.6200.

General Procedure for the synthesis of 2-(4-(benzyloxy) phenyl)-5-(4-(octyloxy) phenyl)-1,3, 4-thiadiazole (7)$^3$:  

4-benzyloxy benzoic acid (2.5mmol) in 6 ml of thionyl chloride and catalytic amount of DMF was refluxed for 4 h. The excess of thionyl chloride was removed by distillation and then the crude product was dried in vacuo and used for the next reaction without further purification and characterization.

A solution of 4-benzyloxy benzoic acid chloride (2.2 mmol, 1equiv.) in THF was added dropwise into a solution of ethyl 4-n-octyloxy benzohydrazide (15a) (2.31 mmol, 1.05equiv.) and triethylamine (2.2mmol, 1equiv.) in THF. The reaction mixture was refluxed for 24 h. After cooling to room temperature, THF was evaporated in rotavapor and the residue was extracted with ethyl acetate and concentratin. The resulting crude product (8a) was directly used for next reaction. The crude product 8a (0.3mmol, 1equiv.) was treated with lawesson’s reagent indry toluene and refluxed for 24 h. The residue was slowly added to ice water and extracted with DCM. The combine extract was washed with brine, dried over anhydrous Na$_2$SO$_4$ and then concentrated. Then, the crude product was further purified through column chromatography on neutral alumina. Elution with 60-70% DCM-hexane produced the require product.

7:$R_f$= 0.35 (70% DCM-hexane); white solid; yield: 45%; IR (KBr pellet): $\nu$ max in cm$^{-1}$3444, 2919, 2851, 1583, 1444, 1422, 1382, 1238, 1126, 1065; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.92 (d, 4H, $J = 12$Hz, H$_{Ar}$), 7.44 (t, 2H, $J = 6$Hz, H$_{Ar}$), 7.40 (d, 2H, $J = 12$ Hz, H$_{Ar}$), 7.36 (d, 1H, $J = 12$Hz, H$_{Ar}$), 7.07 (d, 2H, $J = 18$Hz, H$_{Ar}$), 6.98 (d, 2H, $J = 12$ Hz, H$_{Ar}$), 5.14 (s, 2H, OCH$_2$Ph), 4.02(t, 2H, $J = 6$ Hz, OCH$_2$), 1.79-1.83 (m, 2H, CH$_2$),1.47 (m, 2H, CH$_2$), 1.29-1.33 (m, 8H, 4×CH$_2$), 0.89 (t, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 167.19, 166.55, 161.62, 161.10, 136.55, 129.59, 129.56, 128.90, 128.41, 127.69, 115.60, 115.21, 70.37, 68.48, 32.02, 29.55,
29.44, 29.36, 26.22, 22.87, 14.32; HRMS (+APCI) exact mass calculated for C_{29}H_{33}N_{2}O_{2}S (M+H^+): 473.2263, Found: 473.2260.

General Procedure for the synthesis of 4-(5-(4-(octylxylo) phenyl)-1, 3, 4-thiadiazol-2-yl) phenol (6): 5.

2-(4-(benzyloxy) phenyl)-5-(4-(alkoxy) phenyl)-1, 3, 4-oxadiazole (7) was dissolved in dry THF and degassed with nitrogen for 10-15 minutes. Then, 10 mol% of Pd/C was added to the above reaction mixture. The reaction was carried out under H_{2} gas overnight. After the reaction was completed, mixture was filtered in celite bed to remove Pd/C and washed with ethyl acetate. The filtrate was concentrated and then the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 60% EtOAc-hexanes produced the require product.

6: R_f = 0.30 (70% EtOAc-hexane); white solid; yield: 60%; IR (KBr pellet): \nu_{\text{max}} \text{ in cm}^{-1} 3444, 2919, 2850, 1582, 1466, 1382, 1239, 1122, 1010; ^1H NMR (CDCl_{3}, 600 MHz): \delta 7.90 (d, 4H, J = 12 Hz, H_{Ar}), 6.98 (d, 4H, J = 6Hz, H_{Ar}), 6.14 (br s, 1H, OH), 4.02 (t, 2H, OCH_{2}), 1.79-1.83 (m, 2H, 1×CH_{2}), 1.47 (m, 2H, CH_{2}), 1.24-1.29 (m, 8H, 4×CH_{2}), 0.88 (t, 3H, CH_{3}); ^13C NMR (CDCl_{3}, 150 MHz): \delta 175.52, 168.72, 161.74, 160.01, 130.54, 129.28, 119.29, 117.08, 116.30, 114.96, 68.39, 32.10, 2.78, 29.76, 29.59, 29.53, 26.22, 22.89, 14.33; HRMS (+APCI) exact mass calculated for C_{22}H_{27}N_{2}O_{2}S (M+H^+): 383.1793, Found: 383.1787.

Procedure for the synthesis of 2-n/8: 6.

A mixture of appropriate compound (6) (1.1 mmol, 1.1 equiv.), anhydrous K_{2}CO_{3} (2.2mmol, 2.2 equiv.), cholesteryl \omega-bromoalkanoate (1 mmol, 1 equiv.) were taken in dry DMF and heated under argon atmosphere at 70 °C-80 °C for 24 h. After the reaction time was completed, the reaction mixture was poured into ice water and then extracted with DCM. The combine extract was washed with brine, dried over anhydrous Na_{2}SO_{4} and then concentrated. The crude product
was purified by column chromatography on neutral alumina. Elution with 50-60% DCM-hexane produced the require product.

**2-3/8:** $R_f = 0.5$ (60% DCM-hexane); white solid; yield: 82%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3198, 2919, 2851, 1639, 1509, 1468, 1444, 1423, 1238, 1126; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.92 (d, 4H, J = 6Hz, H$_{Ar}$), 6.98 (d, 4H, J = 6Hz, H$_{Ar}$), 5.37 (d, 1H, J = 6Hz, 1 × olefinic H), 4.64 (m, 1H, 1 × CHOCO), 4.02 – 4.08 (m, 4H, 2 × OCH$_2$), 2.51 (m, 2H, 1 × CH$_2$), 2.32 (m, 2H, 1 × CH$_2$), 1.29 – 2.14 (m, 40H, 17 × CH$_2$, 6 × CH), 1.25 (s, 3H, 1 × CH$_3$), 1.14 (d, 3H, J = 6Hz, 1 × CH$_3$), 1.01 (s, 3H, 1 × CH$_3$), 0.90 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.67 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 172.72, 167.45, 167.27, 161.63, 161.28, 139.81, 131.10, 129.58, 123.29, 122.95, 115.22, 74.39, 68.48, 67.23, 56.90, 56.34, 50.23, 42.52, 39.93, 39.73, 38.35, 37.18, 36.80, 36.39, 36.00, 32.12, 32.06, 32.01, 31.25, 29.91, 29.55, 29.44, 29.36, 28.44, 28.22, 28.02, 26.22, 24.79, 24.49, 24.03, 23.03, 22.86, 22.77, 21.24, 19.52, 18.92, 14.31, 12.06; MALDI-TOF exact mass calculated for C$_{53}$H$_{76}$N$_2$O$_4$S(M$^+$): 836.5526, Found: 836.659.

**2-4/8:** $R_f = 0.5$ (60% DCM-hexane); white solid; yield: 78%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3445, 2920, 2850, 1594, 1520, 1465, 1388, 1273, 1138, 1016; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.92 (d, 4H, J = 6Hz, H$_{Ar}$), 6.98 (d, 4H, J = 6Hz, H$_{Ar}$), 5.36 (d, 1H, J = 6Hz, 1 × olefinic H), 4.62 (s, 1H, 1 × CHOCO), 4.02 – 4.05 (m, 4H, 2 × OCH$_2$), 2.31 – 2.38 (m, 4H, 2 × CH$_2$), 1.29 – 2.00 (m, 42H, 18 × CH$_2$, 6 × CH), 1.25 (s, 3H, 1 × CH$_3$), 1.09 (d, 3H, J = 6Hz, 1 × CH$_3$), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.67 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 173.02, 167.41, 167.29, 161.62, 161.35, 139.83, 129.57, 123.17, 122.98, 122.90, 115.22, 74.18, 68.48, 67.84, 56.88, 56.33, 50.22, 42.51, 39.92, 39.73, 38.35, 37.18, 36.80, 36.39, 35.99, 34.46, 32.11, 32.01, 29.55, 29.44, 29.36, 28.72, 28.43, 28.22, 28.01, 26.22, 24.48, 23.03, 22.77, 18.91, 14.31, 12.05; MALDI-TOF exact mass calculated for C$_{54}$H$_{78}$N$_2$O$_4$S(M$^+$): 850.5682, Found: 850.8520.

**2-5/8:** $R_f = 0.5$ (60% DCM-hexane); white solid; yield: 75%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$ 3445, 2920, 2850, 1594, 1520, 1465, 1388, 1273, 1138, 1016; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 7.92 (d, 4H, J = 12Hz, H$_{Ar}$), 6.98 (d, 4H, J = 6Hz, H$_{Ar}$), 5.37 (s, 1H, 1 × olefinic H), 4.61 – 4.63 (m, 1H, 1 × CHOCO), 4.00 – 4.05 (m, 4H, 2 × OCH$_2$), 2.38 – 2.40 (m, 4H, 1 × CH$_2$), 2.29 – 2.31 (m, 2H, 1 × CH$_2$), 1.04 – 2.01 (m, 42H, 18 × CH$_2$, 6 × CH), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (s, 3H, 1 × CH$_3$),
0.9 (d, 3H, J = 6Hz, 1 × CH₃), 0.87 (d, 3H, J = 6Hz, 1 × CH₃), 0.86 (d, 3H, J = 6Hz, 1 × CH₃), 0.67 (s, 3H, 1 × CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 173.02, 167.42, 167.30, 161.63, 161.36, 139.84, 129.58, 123.18, 122.99, 122.90, 115.23, 74.19, 68.49, 67.85, 56.89, 56.34, 50.23, 39.93, 39.74, 38.36, 37.19, 36.40, 36.00, 34.66, 32.02, 29.55, 29.45, 29.36, 28.73, 28.44, 28.23, 28.02, 26.23, 24.48, 24.04, 23.04, 22.87, 22.78, 21.89, 21.24, 19.53, 14.32, 12.06; MALDI-TOF exact mass calculated for C₅₅H₈₀N₂O₄S(M⁺): 864.5839, Found: 864.738.

2-7/8: R₂ = 0.5 (60% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): ν_max in cm⁻¹ 3444, 2920, 2849, 1588, 1454, 1424, 1390, 1258, 1226, 966; ¹H NMR (CDCl₃, 600 MHz): δ 7.91 (d, 4H, J = 12Hz, H_Ar), 6.98 (d, 4H, J = 6Hz, H_Ar), 5.36 (s, 1H, olefinic H), 4.60 – 4.62 (m, 1H, 1 × CHOCO), 4.02 (t, 4H, J = 6Hz, 2 × OCH₂), 2.26 – 2.31 (m, 4H, 2 × CH₂), 1.28 – 2.01 (m, 48H, 21 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.90 (d, 3H, J = 6Hz, 1 × CH₃), 0.87 (s, 3H, 1 × CH₃), 0.85 (d, 3H, J = 6Hz, 1 × CH₃), 0.66 (s, 3H, 1 × CH₃); ¹³C NMR (CDCl₃, 150 MHz): δ 173.39, 167.29, 161.56, 161.51, 139.85, 129.51, 122.99, 122.96, 122.80, 115.16, 73.93, 68.44, 68.31, 56.86, 56.32, 50.20, 42.49, 39.91, 39.71, 38.36, 37.18, 36.78, 36.37, 35.99, 32.09, 32.01, 29.90, 29.55, 29.43, 29.35, 29.25, 29.16, 28.21, 26.21, 24.04, 23.02, 22.86, 22.77, 18.91, 12.04; MALDI-TOF exact mass calculated for C₅₇H₈₄N₂O₄S(M⁺): 892.6152, Found: 892.2309.

General Procedure for the synthesis of 4-n-alkoxy benzonitrile (14)⁴:

A mixture of ethyl 4-hydroxybenzonitrile (9.05 mmol, 1equiv.), anhydrous K₂CO₃ (19.91mmol, 2.2 equiv.), n-bromoocctane (9.95 mmol, 1.1 equiv.) were taken in dry DMF and heated at 70°C-80°C for 24h under argon atmosphere. After the reaction time was completed, the reaction mixture was poured into ice water and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous Na₂SO₄ and then concentrated. The crude product was purified by column chromatography on silica. Elution with hexane followed by 5-10% ethyl acetate-hexane produced the require product.

14: R₂ = 0.35 (10% EtOAc-hexane); colorless liquid; yield: 85%; IR (KBr pellet): ν_max in cm⁻¹ 2920, 2850, 2220, 1597, 1518, 1467, 1422, 1278, 1242, 1138; ¹H NMR (CDCl₃, 400 MHz): δ 7.57 (d, 2H, J = 8Hz, H_Ar), 6.93 (d, 2H, J = 8Hz, H_Ar), 3.99 (t, 2H, J = 4 Hz, OCH₂), 1.76-1.83
(m, 2H, CH₂), 1.41-1.46 (m, 2H, CH₂), 1.28-1.33 (m, 8H, 4×CH₂), 0.88 (t, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 162.62, 134.10, 119.51, 115.33, 103.74, 68.58, 31.95, 29.45, 29.37, 29.14, 26.10, 22.82, 14.27; ¹³C NMR (CDCl₃, 100 MHz): δ 162.62, 134.10, 119.51, 115.33, 103.74, 68.58, 31.95, 29.45, 29.37, 29.14, 26.10, 22.82, 14.27; HRMS (+APCI) exact mass calculated for C₁₅H₂₂NO (M+H⁺): 232.1701, Found: 232.1701.

General Procedure for the synthesis of 4-(alkoxy)-N'-hydroxybenzamidine (13)⁴:
To a stirred solution of 4-n-octyloxy benzonitrile (14) (9mmol, 1equiv.) in ethanol (20ml) was added hydroxylamine hydrochloride (19.8 mmol, 2.2 equiv.) and then triethylamine (20.7 mmol, 2.3 equiv.). The solution was stirred under reflux for 18h and then diluted with water. Ethanol was removed under reduced pressure and the aqueous layer extracted 2 times with DCM. The combined organic phases were dried over Na₂SO₄, evaporated under reduced pressure as the residue purified by recrystallization (ethanol) to afford the title compound as a white solid.

13: Rᵣ = 0.25 (30% EtOAc-hexane); white solid; yield: 78%; IR (KBr pellet): νmax in cm⁻¹ 3448, 3350, 2921, 2852, 1652, 1610, 1519, 1390, 1251, 826; ¹H NMR (CDCl₃, 400 MHz): δ 7.55 (d, 2H, J = 4Hz, HAr), 6.88 (d, 2H, J = 4Hz, HAr), 4.83 (s, 2H, NH₂), 3.97 (t, 2H, J = 4Hz, OCH₂), 1.76-1.80 (m, 2H, CH₂), 1.41-1.46 (m, 2H, CH₂), 1.28-1.31 (m, 8H, 4×CH₂), 0.88 (t, 3H, CH₃); ¹³C NMR (CDCl₃, 100 MHz): δ 160.81, 152.87, 127.37, 124.84, 114.75, 68.34, 32.02, 29.56, 29.44, 29.40, 26.23, 22.86, 14.30; HRMS (+APCI) exact mass calculated for C₁₅H₂₅N₂O₂ (M+H⁺): 265.1916, Found: 265.1907.

General Procedure for the synthesis of 3-(4-(benzyloxy) phenyl)-5-(4-(alkoxy) phenyl)-1, 2, 4-oxadiazole (10)⁴:
4-benzoyloxy benzoic acid (2.5mmol) in 6 ml of thionyl chloride and catalytic amount of DMF was refluxed for 4 h. The excess of thionyl chloride was removed by distillation and then the crude product was dried in vacuo and used for the next reaction without further purification and characterization.

A mixture of 4-(octyloxy)-N'-hydroxybenzamidine (2.42mmol, 1.1 equiv.) and dry pyridine was stirred under Argon atmosphere at 0°C. To this, a solution of 4-benzoyloxy benzoic acid chloride (2.2 mmol, 1equiv.) in dry THF was added drop wise. The reaction mixture was refluxed for 24
h and then poured into cold water. The whole mass was extracted with Chloroform. The combined extracts were washed with water, brine, dried over anhyd. Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on neutral alumina. Elution with 60-70% CH$_2$Cl$_2$ hexanes yielded the desired product.

10: $R_f$= 0.4 (50% DCM-hexane); off white solid; yield: 75%; IR (KBr pellet): $v_{max}$ in cm$^{-1}$ 2921, 2851, 1607, 1516, 1468, 1306, 1255, 1174, 1037, 831; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.15 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 8.08 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 7.45 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 7.41 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 7.36 (t, 1H, $J$ = 6Hz, H$_{Ar}$), 7.11 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 7.00 (d, 2H, $J$ = 6Hz, H$_{Ar}$), 5.16 (s, 2H, -ArCH$_2$), 4.02 (t, 2H, $J$ = 6 Hz, OCH$_2$), 1.79-1.84 (m, 2H, CH$_2$), 1.45-1.50 (m, 2H, CH$_2$), 1.26-1.38 (m, 8H, 4×CH$_2$), 0.89 (t, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 175.42, 168.75, 162.39, 161.66, 136.27, 130.25, 129.24, 128.92, 128.50, 127.73, 119.55, 117.39, 115.49, 114.89, 70.38, 68.34, 32.01, 29.55, 29.43, 29.37, 26.21, 22.85, 14.31; HRMS (+APCI) exact mass calculated for C$_{29}$H$_{33}$N$_2$O$_3$ (M+H$^+$): 457.2491, Found: 57.2441.

General Procedure for the synthesis of 4-(5-(4-octyloxy) phenyl)-1, 2, 4-oxadiazol-3-yl) phenol (9):

3-(4-(benzyloxy) phenyl)-5-(4-octyloxy) phenyl)-1, 2, 4-oxadiazole (10) was dissolved in dry THF and degassed with nitrogen for 10-15 minutes. Then, 10 mol% of Pd/C was added to the above reaction mixture. The reaction was carried out under H$_2$ gas overnight. After the reaction was completed, mixture was filtered in celite bed to remove Pd/C and washed with ethyl acetate. The filtrate was concentrated and then the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 40% EtOAc-hexanes produced the require product.

9: $R_f$= 0.2 (70% EtOAc-hexane); white solid; yield: 60%; IR (KBr pellet): $v_{max}$ in cm$^{-1}$ 3104, 2922, 2851, 1612, 1497, 1391, 1290, 1262, 1174, 844; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.14 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 7.97 (d, 2H, $J$ = 12Hz, H$_{Ar}$), 6.87 (d, 2H, $J$ = 6Hz, H$_{Ar}$), 6.79 (d, 2H, $J$ = 6Hz, H$_{Ar}$), 3.92 (t, 2H, J = 6 Hz, OCH$_2$), 2.49-2.52 (m, 2H, CH$_2$), 1.70-1.72 (m, 2H, CH$_2$), 1.16-1.24 (m, 8H, 4×CH$_2$), 0.78 (t, 3H, CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 179.68, 165.90, 162.57, 161.07, 131.80, 129.70, 116.35, 115.10, 114.81, 114.44, 68.36, 31.88, 29.42, 29.30, 29.22, 26.08,
22.73, 14.22; HRMS (+APCI) exact mass calculated for C_{22}H_{27}N_{2}O_{3} (M+H\textsuperscript{+}): 367.2022, Found: 367.1603.

Procedure for the synthesis of 3-n/8\textsuperscript{6}:

A mixture of appropriate compound (9) (1.1 mmol, 1.1 equiv.), anhydrous K\textsubscript{2}CO\textsubscript{3} (2.2 mmol, 2.2 equiv.), cholesteryl \(\omega\)-bromoalkanoate (1 mmol, 1 equiv.) were taken in dry DMF and heated under argon atmosphere at 70\(^\circ\)C-80\(^\circ\)C for 24 h. After the reaction time was completed, the reaction mixture was poured into ice water and then extracted with DCM. The combine extract was washed with brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and then concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with 40-50% DCM-hexane produced the require product.

**3-3/8:** \(R_f = 0.55\) (60% DCM-hexane); white solid; yield: 67%; IR (KBr pellet): \(\nu_{\text{max}}\) in cm\(^{-1}\) 3444, 2937, 2851, 1742, 1611, 1503, 1471, 1421, 1364, 838; \(^1\)H NMR (CDCl\textsubscript{3}, 600 MHz): \(\delta\) 8.14 (d, 2H, \(J = 6\) Hz, H\textsubscript{Ar}), 8.08 (d, 2H, \(J = 6\) Hz, H\textsubscript{Ar}), 7.00 (t, 2H, \(J = 6\) Hz, H\textsubscript{Ar}), 5.37 (s, 1H, 1 × olefinic H), 4.64 (s, 1H, 1 × CHOCO), 4.02 - 4.11 (m, 4H, 2 × OCH\textsubscript{2}), 2.52 (m, 2H, 1 × CH\textsubscript{2}), 2.32 (m, 2H, 1 × CH\textsubscript{2}), 1.33 - 2.15 (m, 40H, 17 × CH\textsubscript{2}, 6 × CH), 1.30 (s, 3H, 1 × CH\textsubscript{3}), 1.16 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 0.91 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 0.86 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 0.67 (s, 3H, 1 × CH\textsubscript{3}); \(^{13}\)C NMR (CDCl\textsubscript{3}, 150 MHz): \(\delta\) 175.49, 172.65, 168.79, 162.60, 161.70, 139.80, 130.25, 129.28, 122.96, 119.56, 117.25, 115.15, 114.94, 74.42, 68.39, 67.32, 56.91, 56.36, 50.25, 42.54, 39.95, 39.74, 38.37, 28.23, 28.04, 26.25, 24.77, 23.03, 22.87, 22.77, 21.25, 19.53, 18.93, 14.30, 12.06; MALDI-TOF exact mass calculated for C\textsubscript{53}H\textsubscript{77}N\textsubscript{2}O\textsubscript{5} (M+H\textsuperscript{+}): 821.5832, Found: 821.2350.

**3-4/8:** \(R_f = 0.55\) (60% DCM-hexane); white solid; yield: 73%; IR (KBr pellet): \(\nu_{\text{max}}\) in cm\(^{-1}\) 3444, 2938, 2851, 1741, 1611, 1503, 1364, 1256, 1172, 763; \(^1\)H NMR (CDCl\textsubscript{3}, 600 MHz): \(\delta\) 8.14 (d, 2H, \(J = 6\) Hz, H\textsubscript{Ar}), 8.08 (d, 2H, \(J = 6\) Hz, H\textsubscript{Ar}), 7.00 (t, 4H, \(J = 6\) Hz, H\textsubscript{Ar}), 5.36 (s, 1H, 1 × olefinic H), 4.62 (s, 1H, 1 × CHOCO), 4.02 - 4.07 (m, 4H, 2 × OCH\textsubscript{2}), 2.31 - 2.38 (m, 4H, 2 × CH\textsubscript{2}), 1.33 - 2.00 (m, 42H, 18 × CH\textsubscript{2}, 6 × CH), 1.30 (s, 3H, 1 × CH\textsubscript{3}), 1.13 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 1.01 (s, 3H, 1 × CH\textsubscript{3}), 0.94 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 0.86 (d, 3H, \(J = 6\) Hz, 1 × CH\textsubscript{3}), 0.66 (s, 3H, 1 × CH\textsubscript{3}); \(^{13}\)C NMR (CDCl\textsubscript{3}, 150 MHz): \(\delta\) 175.56, 172.65, 168.74, 162.86, 161.66, 139.87, 130.21, 129.25, 122.84, 119.57, 116.92, 115.11, 114.90, 73.97, 68.36, 56.88, 56.33,
50.22, 42.51, 39.93, 38.38, 37.20, 36.80, 36.39, 36.01, 34.85, 32.11, 32.06, 29.79, 29.61, 29.54, 29.41, 29.18, 28.23, 28.04, 26.24, 26.02, 25.14, 24.49, 24.05, 23.04, 22.90, 22.78, 21.24, 19.53, 18.93, 14.34, 12.06; MALDI-TOF exact mass calculated for C$_{54}$H$_{79}$N$_2$O$_5$(M+H$^+$): 835.5989, Found: 835.77.

3-5/8: $R_f = 0.55$ (60% DCM-hexane); white solid; yield: 70%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$: 3444, 2937, 2846, 1752, 1711, 1593, 1421, 1301, 1224, 838; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.13 (d, 2H, J = 12Hz, H$_{Ar}$), 8.08 (d, 2H, J = 6Hz, H$_{Ar}$), 7.00 (t, 4H, J = 12Hz, H$_{Ar}$), 5.37 (d, 1H, 1 × olefinic H), 4.61 – 4.63 (m, 1H, 1 × CHOCO), 4.00 - 4.07 (m, 4H, 2 × OCH$_2$), 3.37 – 3.40 (m, 2H, 1 × CH$_2$), 2.29 – 2.31 (m, 2H, 1 × CH$_2$), 1.23 – 2.01 (m, 44H, 19 × CH$_2$, 6 × CH), 1.09 (d, 3H, J = 6Hz, 3 × CH$_3$), 0.91 (d, 3H, J = 6Hz, 3 × CH$_3$), 0.87 (d, 3H, J = 6Hz, 3 × CH$_3$), 0.86 (d, 3H, J = 6Hz, 3 × CH$_3$), 0.84 (d, 3H, J = 6Hz, 3 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 175.54, 173.44, 168.73, 162.87, 161.66, 139.86, 134.16, 130.21, 129.25, 122.84, 119.54, 116.94, 115.37, 115.10, 114.89, 73.95, 68.40, 68.35, 50.20, 42.50, 39.91, 39.72, 38.36, 36.38, 36.00, 32.02, 29.92, 29.57, 29.45, 29.40, 29.21, 29.17, 28.43, 28.23, 28.02, 26.00, 24.04, 23.04, 22.87, 22.78, 19.52, 14.32, 12.05; MALDI-TOF exact mass calculated for C$_{55}$H$_{81}$N$_2$O$_5$(M+H$^+$): 849.6145, Found: 849.0156.

3-7/8: $R_f = 0.55$ (60% DCM-hexane); white solid; yield: 72%; IR (KBr pellet): $\nu_{\text{max}}$ in cm$^{-1}$: 3444, 2937, 2851, 1742, 1611, 1503, 1471, 1421, 1364, 838; $^1$H NMR (CDCl$_3$, 600 MHz): $\delta$ 8.13 (d, 2H, J = 12Hz, H$_{Ar}$), 8.08 (d, 2H, J = 6Hz, H$_{Ar}$), 7.00 (t, 4H, J = 6Hz, H$_{Ar}$), 5.36 (s, 1H, 1 × olefinic H), 4.62 (s, 1H, 1 × CHOCO), 4.02 - 4.03 (m, 4H, 2 × OCH$_2$), 2.37 – 2.40 (m, 4H, 2 × CH$_2$), 1.32 – 2.30 (m, 48H, 21 × CH$_2$, 6 × CH), 1.30 (s, 3H, 1 × CH$_3$), 1.13 (d, 3H, J = 6Hz, 1 × CH$_3$), 1.01 (s, 3H, 1 × CH$_3$), 0.91 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.86 (d, 3H, J = 6Hz, 1 × CH$_3$), 0.67 (s, 3H, 1 × CH$_3$); $^{13}$C NMR (CDCl$_3$, 150 MHz): $\delta$ 175.57, 173.44, 168.77, 162.89, 161.68, 139.90, 130.23, 129.27, 122.85, 119.59, 116.98, 115.13, 114.92, 68.42, 68.39, 56.89, 56.35, 50.24, 36.81, 36.40, 30.07, 29.57, 29.45, 29.42, 29.23, 29.17, 28.44, 28.23, 28.04, 26.25, 25.14, 19.52, 18.92, 12.06; MALDI-TOF exact mass calculated for C$_{57}$H$_{83}$N$_2$O$_5$(M+H$^+$): 877.6458, Found: 877.7493.
(4) NMR Data:

Figure S1. $^1$H NMR (600 MHz) spectra of 1-3/8 in CDCl$_3$

Figure S2. $^{13}$C NMR (150 MHz) spectra of 1-3/8 in CDCl$_3$
**Figure S3.** $^1$H NMR (600 MHz) spectra of 1-4/8 in CDCl$_3$

**Figure S4.** $^{13}$C NMR (150 MHz) spectra of 1-4/8 in CDCl$_3$
Figure S5. $^1$H NMR (600 MHz) spectra of 1-5/8 in CDCl$_3$

Figure S6. $^{13}$C NMR (150 MHz) spectra of 1-5/8 in CDCl$_3$
Figure S7. $^1$H NMR (600 MHz) spectra of 1-7/8 in CDCl$_3$

Figure S8. $^{13}$C NMR (150 MHz) spectra of 1-7/8 in CDCl$_3$
**Figure S9.** $^1$H NMR (600 MHz) spectra of 1-3/9 in CDCl$_3$

**Figure S10.** $^{13}$C NMR (150 MHz) spectra of 1-3/9 in CDCl$_3$
Figure S11. $^1$H NMR (600 MHz) spectra of 1-4/9 in CDCl₃

Figure S12. $^{13}$C NMR (150 MHz) spectra of 1-4/9 in CDCl₃
Figure S13. $^1$H NMR (600 MHz) spectra of 1-5/9 in CDCl$_3$

Figure S14. $^{13}$C NMR (150 MHz) spectra of 1-5/9 in CDCl$_3$
Figure S15. $^1$H NMR (600 MHz) spectra of 1-7/9 in CDCl$_3$.

Figure S16. $^{13}$C NMR (150 MHz) spectra of 1-7/9 in CDCl$_3$. 
Figure S17. $^1$H NMR (600 MHz) spectra of 1-3/10 in CDCl$_3$

Figure S18. $^{13}$C NMR (150 MHz) spectra of 1-3/10 in CDCl$_3$
Figure S19. $^1$H NMR (600 MHz) spectra of 1-4/10 in CDCl$_3$

Figure S20. $^{13}$C NMR (150 MHz) spectra of 1-4/10 in CDCl$_3$
Figure S21. $^1$H NMR (600 MHz) spectra of 1-5/10 in CDCl$_3$

Figure S22. $^{13}$C NMR (150 MHz) spectra of 1-5/10 in CDCl$_3$
Figure S23. $^1$H NMR (600 MHz) spectra of 1-7/10 in CDCl$_3$

Figure S24. $^{13}$C NMR (150 MHz) spectra of 1-7/10 in CDCl$_3$
Figure S25. $^1$H NMR (600 MHz) spectra of 2-3/8 in CDCl$_3$

Figure S26. $^{13}$C NMR (150 MHz) spectra of 2-3/8 in CDCl$_3$
Figure S27. $^1$H NMR (600 MHz) spectra of 2-4/8 in CDCl$_3$

Figure S28. $^{13}$C NMR (150 MHz) spectra of 2-4/8 in CDCl$_3$
Figure S29. $^1$H NMR (600 MHz) spectra of 2-5/8 in CDCl$_3$

Figure S30. $^{13}$C NMR (150 MHz) spectra of 2-5/8 in CDCl$_3$
Figure S31. $^1$H NMR (600 MHz) spectra of 2-7/8 in CDCl$_3$.

Figure S32. $^{13}$C NMR (150 MHz) spectra of 2-7/8 in CDCl$_3$. 
Figure S33. $^1$H NMR (600 MHz) spectra of 3-3/8 in CDCl$_3$.

Figure S34. $^{13}$C NMR (150 MHz) spectra of 3-3/8 in CDCl$_3$. 
**Figure S35.** $^1$H NMR (600 MHz) spectra of 3-4/8 in CDCl$_3$

**Figure S36.** $^{13}$C NMR (150 MHz) spectra of 3-4/8 in CDCl$_3$
Figure S37. $^1$H NMR (600 MHz) spectra of 3-5/8 in CDCl$_3$

Figure S38. $^{13}$C NMR (150 MHz) spectra of 3-5/8 in CDCl$_3$
Figure S39. $^1$H NMR (600 MHz) spectra of 3-7/8 in CDCl$_3$

Figure S40. $^{13}$C NMR (150 MHz) spectra of 3-7/8 in CDCl$_3$
Figure S41. $^1$H NMR (600 MHz) spectra of 4a in CDCl$_3$

Figure S42. $^{13}$C NMR (150 MHz) spectra of 4a in CDCl$_3$
Figure S43. $^1$H NMR (600 MHz) spectra of 4b in CDCl$_3$

Figure S44. $^{13}$C NMR (150 MHz) spectra of 4b in CDCl$_3$
Figure S45. $^1$H NMR (600 MHz) spectra of 4c in CDCl$_3$

Figure S46. $^{13}$C NMR (150 MHz) spectra of 4c in CDCl$_3$
Figure S47. $^1$H NMR (600 MHz) spectra of 5a in CDCl$_3$

Figure S48. $^{13}$C NMR (150 MHz) spectra of 5a in CDCl$_3$
Figure S49. $^1$H NMR (600 MHz) spectra of 5b in CDCl$_3$

Figure S50. $^{13}$C NMR (150 MHz) spectra of 5b in CDCl$_3$
Figure S5. $^1$H NMR (600 MHz) spectra of 5c in CDCl$_3$

Figure S52. $^{13}$C NMR (150 MHz) spectra of 5c in CDCl$_3$
**Figure S53.** $^1$H NMR (400 MHz) spectra of 6 in CDCl$_3$

**Figure S54.** $^{13}$C NMR (100 MHz) spectra of 6 in CDCl$_3$
**Figure S55.** $^1$H NMR (400 MHz) spectra of 7 in CDCl$_3$

**Figure S56.** $^{13}$C NMR (100 MHz) spectra of 7 in CDCl$_3$
Figure S57. $^1$H NMR (600 MHz) spectra of 9 in CDCl$_3$.

Figure S58. $^{13}$C NMR (150 MHz) spectra of 9 in CDCl$_3$.
**Figure S59.** $^1$H NMR (600 MHz) spectra of 10 in CDCl$_3$

**Figure S60.** $^{13}$C NMR (150 MHz) spectra of 10 in CDCl$_3$
**Figure S61.** $^1$H NMR (600 MHz) spectra of 11 in DMSO

**Figure S62.** $^{13}$C NMR (150 MHz) spectra of 11 in DMSO
Figure S63. $^{13}$C NMR (150 MHz) spectra of 12 in CDCl$_3$

Figure S64. $^1$H NMR (600 MHz) spectra of 12 in CDCl$_3$
Figure S65. $^1$H NMR (600 MHz) spectra of 13 in CDCl$_3$

Figure S66. $^{13}$C NMR (150 MHz) spectra of 13 in CDCl$_3$
Figure S67. $^1$H NMR (600 MHz) spectra of 14 in CDCl$_3$

Figure S68. $^{13}$C NMR (150 MHz) spectra of 14 in CDCl$_3$
**Figure S69.** $^1$H NMR (400 MHz) spectra of 15a in CDCl$_3$

**Figure S70.** $^{13}$C NMR (100 MHz) spectra of 15a in CDCl$_3$
Figure S71. $^1$H NMR (400 MHz) spectra of 15b in CDCl$_3$

Figure S72. $^{13}$C NMR (100 MHz) spectra of 15b in CDCl$_3$
Figure S73. $^1$H NMR (400 MHz) spectra of 15c in CDCl$_3$

Figure S74. $^{13}$C NMR (100 MHz) spectra of 15c in CDCl$_3$
Figure S75. $^1$H NMR (400 MHz) spectra of 16a in CDCl$_3$

Figure S76. $^{13}$C NMR (100 MHz) spectra of 16a in CDCl$_3$
**Figure S77.** $^1$H NMR (400 MHz) spectra of 16b in CDCl$_3$

**Figure S78.** $^{13}$C NMR (100 MHz) spectra of 16b in CDCl$_3$
Figure S79. $^1$H NMR (400 MHz) spectra of 16c in CDCl$_3$

Figure S80. $^{13}$C NMR (100 MHz) spectra of 16c in CDCl$_3$
(5) Thermal behavior

Figure S81. DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-3/8 (a); focal conic texture along with homeotropically aligned regions obtained for the SmA phase of compound 1-3/8 at 135 °C (b).

Figure S82. DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-4/8 (a); focal conic texture obtained for the SmA phase of compound 1-4/8 at 139 °C (b).
**Figure S83.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-5/8 (a); POM image obtained after shearing the focal conic texture of the SmA phase of compound 1-5/8 at 149 °C (b) and at 139 °C.

**Figure S84.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-3/9 (a); POM image obtained after shearing the homeotropically aligned SmA phase of compound 1-3/9 at 135 °C (b) and the texture obtained on shearing the same at 135 °C (c).

**Figure S85.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-4/9 (a); POM image obtained for the SmA phase of compound 1-4/9 at 128 °C (b) and at 116 °C (c).
Figure S86. DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-7/9 (a); POM image obtained for the SmA phase of compound 1-7/9 at 70 °C (b).

Figure S87. DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-3/10 (a); POM image obtained for the SmA phase of compound 1-3/10 at 186 °C (b).

Figure S88. DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 1-4/10 (a); POM image obtained for the SmA phase of compound 1-4/10 at 148 °C (b) and SmC* phase at 116 °C.
**Figure S89.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 2-3/8 (a); POM image obtained for the N* phase of compound 2-3/8 at 158 °C (b).

**Figure S90.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 2-4/8 (a); POM image obtained for the SmA phase of compound 2-4/8 at 220 °C (b).

**Figure S91.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 2-5/8 (a); POM image obtained for the BPIII phase of compound 2-5/8 at 219 °C (b) and N* phase at 130 °C.
**Figure S92.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 2-7/8 (a); POM image obtained for the SmA phase of compound 2-7/8 at 191 °C (b).

**Figure S93.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 3-3/8 (a); POM image obtained for the SmA phase of compound 3-3/8 at 176 °C (b).

**Figure S94.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 3-4/8 (a); POM image obtained for the SmA phase of compound 3-4/8 at 176 °C (b).
**Figure S95.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 3-5/8 (a); POM image obtained for the SmA phase of compound 3-5/8 at 141 °C (b).

**Figure S96.** DSC thermogram obtained for the first cooling (blue trace) and second heating (red trace) for compound 3-7/8 (a); POM image obtained for the SmA phase of compound 3-7/8 at 176 °C (b).
**Figure S97.** Bargraph representing the thermal behavior of cholesterol-based dimers (in cooling cycle)
(6) Gelation properties

Table 1. Gelation properties of compound 1-7/8 in various solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Properties</th>
<th>Critical Gel Concentration (wt. %)</th>
<th>$T_{gel}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>Decane</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>Dodecane</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>Hexadecane</td>
<td>G(O)</td>
<td>1.12</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>Benzene</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>m-xylene</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>DCM</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>9</td>
<td>Chloroform</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>10</td>
<td>THF</td>
<td>S</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>11</td>
<td>n-butanol</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>12</td>
<td>Ethanol</td>
<td>P</td>
<td>----</td>
<td>---</td>
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<tr>
<td>13</td>
<td>Methanol</td>
<td>P</td>
<td>----</td>
<td>---</td>
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<tr>
<td>14</td>
<td>DMSO</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>15</td>
<td>DMF</td>
<td>P</td>
<td>----</td>
<td>---</td>
</tr>
</tbody>
</table>

G = stable gel; S = soluble; P = precipitate; O = opaque; The critical gelation concentration (wt. %) is the minimum concentration necessary for gelation; $T_{gel}$ ($^\circ$C) is the thermal stability of the gels determined by ‘dropping ball’ method (weight of the ball is 68.5 mg).
Table 2. Gelation test for 1,3,4-oxadiazoles, 1,3,4-thiadiazoles and 1,2,4-oxadiazoles in hexadecane.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Properties</th>
<th>CGC (wt.%)</th>
<th>T_{gel}(^\circ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-7/8</td>
<td>G(O)</td>
<td>1.12</td>
<td>52</td>
</tr>
<tr>
<td>1-5/8</td>
<td>G(O)</td>
<td>1.05</td>
<td>53</td>
</tr>
<tr>
<td>1-4/8</td>
<td>G(O)</td>
<td>1.15</td>
<td>52</td>
</tr>
<tr>
<td>1-3/8</td>
<td>G(O)</td>
<td>1.20</td>
<td>52</td>
</tr>
<tr>
<td>2-7/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2-5/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2-4/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>2-3/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>3-7/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>3-5/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>3-4/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>3-3/8</td>
<td>P</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

G = stable gel; P = precipitate; O = opaque; The critical gelation concentration (wt. %) is the minimum concentration necessary for gelation; T_{gel}(^\circ C) is the thermal stability of the gels determined by ‘dropping ball’ method (weight of the ball is 68.5 mg).

Figure S98. Photomicrographs of sol-gel forms of dimers 1-5/8 (a); 1-4/8 (b); 1-3/8 (c) in day light and UV light (365 nm).
(7) References


