
Supplementary Materials

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Experimental

General Information: ^1H and ^{13}C NMR spectra: Bruker AC 300 (300 MHz), Bruker AV 400 (400 MHz), and Bruker ARX 400 (400 MHz), solvents were CDCl_3 , $\text{DMSO}-d_6$. Chemical shifts are expressed as δ values in ppm, coupling constants are given in Hz. Melting points: Büchi HWS SG 200, Stuart Scientific SMP3. DSC: TA Instruments DSC250, IR: JASCO 4100 FT-IR (ATR), FD-MS: Mat 95 (Finnigan); HR-ESI: Agilent 6545 QTOF-HRAM-MS.

UV-vis: Perkin-Elmer Lambda 16. Fluorescence: Perkin-Elmer LS 50B. Polarized optical microscopy: Olympus BX51, ColorView Olympus camera, heat-stage Linkam LTS 350 for temperature regulation. The temperature-dependent wide angle X-ray scattering WAXS with by 14° tilted detector, (sample-detector distance 21 cm, $2\theta_{\text{max}} = 28.5^\circ$) investigations were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). The samples were prepared by fibre extrusion using a mini-extruder. The mini-extruder consisted of a cylindrical stainless steel container of 2 mm diameter with a nozzle of 0.7 mm diameter. The container was heated to the temperature range of the liquid crystal and the fibre was extruded manually via the nozzle with a cylindrical steel pistil. The measurements were carried out in Mark capillaries (Hilgenberg) positioned perpendicular to the incident X-ray beam. All X-ray data was processed and evaluated with the program datasqueeze (<http://www.datasqueezesoftware.com/>) Silver behenate was used as calibration standard for MAXS and WAXS studies. The temperature of the heating stage controls the sample chamber, but the actual sample temperature inside the sealed Mark capillary deviates from this set value because the extruded fibre is surrounded by air. The heating stage was therefore calibrated by measuring the phase-transition temperatures of three known liquid-crystalline internal standards; a linear regression of set versus real transition temperatures was used to convert the set temperatures into corrected sample temperatures. All temperatures reported for the X-ray measurements are these calibrated values.

Synthesis

General procedure A: TOBEs and TOPYs

Pyromellitic dianhydride or pyrazine tetracarboxylic acid (1 eq.) was dissolved in 2 mL of thionyl chloride and a few drops of dimethylformamide were added. The mixture was heated to reflux for 4 hours. The excess of thionyl chloride was removed by addition of 10 mL of dry toluene and subsequent distillation.

The crude acid chloride was dissolved in abs. toluene under nitrogen and was treated with the appropriate alkoxyaryl-tetrazole (4 eq.) and DIPEA (5 eq.). The resulting mixture was heated to reflux for 48 h. The crude reaction mixture was filtered through silica and eluted using toluene/ethylacetate (9/1). The solvent was removed under reduced pressure and the residue was recrystallized from ethyl acetate. The resulting solid was filtrated with suction and washed with cold ethyl acetate.

General procedure B: Tetrazoles from nitriles

3,4-Di(alkyloxy)benzonitrile (1.0 eq.), sodium azide (1.0 eq.) and AlCl_3 (0.1 eq.) were added to 5 mL of NMP and stirred at 170°C overnight. The reaction progress was monitored by thin layer chromatography every 2 hours and, if needed, more NaN_3 and AlCl_3 were added. 50 mL of 2 N HCl was added to the cooled solution and the precipitated solid was filtrated by suction. The crude product was recrystallized from acetonitrile or ethanol and filtrated by suction.

General procedure C: Alkylation of 3,4-Dihydroxybenzonitriles

3,4-Dihydroxybenzonitrile was dissolved in ACN and 3.0 eq. of K_2CO_3 and 2.1 eq. of the corresponding alkyl bromide or alkyl mesylate were added under a nitrogen atmosphere. The reaction mixture was stirred for 2 hours at room temperature and then stirred at 80 °C over night. The reaction progress was monitored by thin layer chromatography. If necessary, further alkyl bromide or alkyl mesylate was added and stirring continued. After the reaction was complete, 2 N HCl was added and the precipitated solid was filtered by suction, or in case the crude product didn't crystallize, the aqueous layer was extracted three times with ethyl acetate. The combined organic phases were washed with brine and dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by recrystallization from petroleum ether. If the product didn't crystallize, it was purified by column chromatography (SiO_2) using petroleum ether/ethyl acetate (20/1) as eluent.

1,2,4,5-Tetrakis(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (10)

According to general procedure A: 44 mg (0.2 mmol, 1 eq.) of pyromellitic dianhydride and 322 mg (0.8 mmol, 4 eq.) (3,4-Di(octyloxy)phenyl)-tetrazole (**7a**) as well as 0.25 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 168 mg (0.1 mmol; 53 %) yellowish solid. **T_m:** 127 – 136 °C. **¹H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.89 (s, 2H), 7.53 – 7.45 (m, 8H), 6.85 (d, J = 8.4 Hz, 4H), 4.00 (dt, J = 15.7, 6.6 Hz, 16H), 1.88 – 1.75 (m, 16H), 1.52 – 1.43 (m, 16H), 1.40 – 1.20 (m, 64H), 0.93 – 0.84 (m, 24H). **¹³C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 166.04, 161.26, 152.67, 149.37, 132.78, 126.07, 120.78, 115.14, 112.78, 111.30, 69.29, 69.11, 31.85, 31.83, 29.73, 29.42, 29.37, 29.30, 29.28, 29.18, 29.08, 26.05, 25.99, 22.70, 22.69, 14.12. **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 2921, 2851, 1605, 1510, 1500, 1475, 1466, 1453, 1389, 1270, 1220, 1135, 1066, 1041, 1017, 964, 809. **FD-MS:** calculated for $C_{102}H_{148}N_8O_{12}$: 1677.12, found: 1677.90.

1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11)

According to general procedure A: 44 mg (0.2 mmol, 1 eq.) of pyromellitic dianhydride and 389 mg (0.8 mmol, 4 eq.) (3,4-Di(decyloxy)phenyl)-tetrazole (**7b**) as well as 0.25 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 72 mg (0.06 mmol; 19 %) yellowish solid. **T_m:** 135 – 148 °C. **¹H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.89 (s, 2H), 7.53 – 7.44 (m, 8H), 6.84 (d, J = 8.4 Hz, 4H), 4.00 (dt, J = 11.7, 6.6 Hz, 16H), 1.91 – 1.74 (m, 16H), 1.57 – 1.41 (m, 16H), 1.28 (q, J = 6.9 Hz, 196H), 0.94 – 0.82 (m, 24H). **¹³C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 166.04, 161.26, 152.67, 149.37, 132.78, 126.06, 120.79, 115.13, 112.77, 111.29, 69.29, 69.10, 31.95, 29.68, 29.64, 29.60, 29.48, 29.43, 29.40, 29.37, 29.18, 29.07, 26.07, 26.00, 22.71, 14.14. **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 2921, 2852, 1604, 1510, 1500, 1467, 1410, 1389, 1270, 1219, 1136, 1074, 1020, 809. **FD-MS:** calculated for $C_{118}H_{180}N_8O_{12}$: 1902.78, found: 1903.05.

1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (12)

According to general procedure A: 44 mg (0.2 mmol, 1 eq.) of pyromellitic dianhydride and 412 mg (0.8 mmol, 4 eq.) (3,4-Di(dodecyloxy)phenyl)-tetrazole (**7c**) as well as 0.25 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 69 mg (0.03 mmol; 16 %) yellowish solid. **T_m:** 122 – 143 °C. **¹H NMR (300 MHz, $CDCl_3$):** δ [ppm] = 8.92 (s, 2H), 7.54 – 7.47 (m, 8H), 6.87 (d, J = 8.4 Hz, 4H), 4.02 (dt, J = 15.7, 6.6), 1.91 – 1.79 (m, 19H), 1.48 (s, 22H), 1.29 (d, J = 6.3 Hz, 190H), 0.94 – 0.86 (m, 36H). **¹³C NMR (75 MHz, $CDCl_3$):** δ [ppm] = 166.04, 161.26, 152.68, 149.38, 132.79, 126.07, 120.78, 115.14, 112.78, 111.30, 69.29, 69.11, 31.95, 29.76, 29.73, 29.71, 29.69, 29.65, 29.49, 29.44, 29.40, 29.19, 29.09, 26.07, 26.01, 22.72, 14.14. **IR (ATR):** $\tilde{\nu}$ [cm^{-1}] = 2920, 2850, 1603, 1559, 1509, 1499, 1466, 1388, 1270, 1219, 1137, 1076, 1011, 809. **FD-MS:** calculated for $C_{134}H_{212}N_8O_{12}$: 2125.62, found: 2125.47.

1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (13)

According to general procedure A: 44 mg (0.2 mmol, 1 eq.) of pyromellitic dianhydride and 389 mg (0.8 mmol, 4 eq.) 5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (**7d**) as well as 0.25 mL DIPEA were dissolved in 10 mL of abs. toluene. **Yield:** 162 mg (0.08 mmol; 43 %) yellowish solid. **T_m:** 93 – 106 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 8.90 (s, 2H), 7.55 – 7.49 (m, 8H), 6.88 (d, J = 9.0 Hz, 4H), 4.07 (dt, J = 13.9, 6.3 Hz, 16H), 1.97 – 1.84 (m, 8H), 1.75 – 1.58 (m, 29H), 1.55 (dtd, J = 13.3, 6.7, 1.8 Hz, 9H), 1.41 – 1.24 (m, 36H), 1.24 – 1.13 (m, 24H), 0.97 (dd, J = 6.4, 3.9 Hz, 24H), 0.89 (dd, J = 6.6, 2.1 Hz, 48H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 166.05, 161.24, 152.66, 149.38, 132.75, 126.11, 120.75, 115.13, 112.66, 111.19, 67.63, 67.49, 39.25, 37.41, 37.38, 37.35, 36.11, 35.99, 35.98, 29.96, 28.00, 24.75, 24.73, 22.72, 22.63, 19.70. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2954, 2926, 2871, 1607, 1506, 1472, 1385, 1268, 1215, 1139, 1019, 741, 708, 676. **FD-MS:** calculated for C₁₁₈H₁₈₀N₈O₁₂: 1901.37, found: 1903.00.

2,3,5,6-Tetrakis(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (14)

According to general procedure A: 102 mg (0.4 mmol, 1 eq.) of pyrazine tetracarboxylic acid and 644 mg (1.6 mmol, 4 eq.) (3,4-Di(octyloxy)phenyl)-tetrazole (**7a**) as well as 0.5 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 512 mg (0.3 mmol; 76 %) yellowish solid. **T_m:** 95 – 118 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.74 – 7.62 (m, 8H), 6.96 (d, J = 8.5 Hz, 4H), 4.08 (td, J = 6.6, 2.8 Hz, 16H), 1.95 – 1.79 (m, 16H), 1.57 – 1.43 (m, 16H), 1.44 – 1.23 (m, 64H), 0.91 (q, J = 3.8 Hz, 24H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 166.65, 159.20, 153.01, 149.40, 139.08, 121.35, 115.01, 112.79, 111.76, 69.38, 69.14, 31.84, 31.82, 29.39, 29.36, 29.28, 29.16, 29.07, 26.03, 25.99, 22.69, 14.12, 14.10. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2923, 2854, 1604, 1559, 1506, 1491, 1466, 1448, 1395, 1261, 1221, 1141, 1074, 1023, 969, 740, 722, 657. **FD-MS:** calculated for C₁₀₀H₁₄₈N₁₀O₁₂: 1681.13, found: 1680.21.

1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (15)

According to general procedure A: 51 mg (0.2 mmol, 1 eq.) of pyrazine tetracarboxylic acid and 389 mg (0.8 mmol, 4 eq.) (3,4-Di(decyloxy)phenyl)-tetrazole (**7b**) as well as 0.25 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 241 mg (0.12 mmol; 63 %) yellowish solid. **T_m:** 90 – 111 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.70 (dd, J = 8.4, 2.0 Hz, 4H), 7.65 (d, J = 2.0 Hz, 4H), 6.96 (d, J = 8.5 Hz, 4H), 4.12 – 4.04 (m, 16H), 1.94 – 1.81 (m, 16H), 1.56 – 1.45 (m, 17H), 1.44 – 1.22 (m, 100H), 0.96 – 0.86 (m, 24H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 166.65, 159.20, 153.02, 149.40, 139.08, 121.35, 115.01, 112.79, 111.76, 69.38, 69.14, 31.94, 29.65, 29.63, 29.61, 29.59, 29.45, 29.41, 29.38, 29.17, 29.08, 26.04, 26.00, 22.71, 14.14, 14.13. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2923, 2852, 1604, 1559, 1540, 1506, 1496, 1467, 1448, 1437, 1395, 1271, 1221, 1170, 1141, 1075, 1025, 988, 738, 723. **FD-MS:** calculated for C₁₁₆H₁₈₀N₁₀O₁₂: 1903.40, found: 1903.05.

1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (16)

According to general procedure A: 51 mg (0.2 mmol, 1 eq.) of pyrazine tetracarboxylic acid and 412 mg (0.8 mmol, 4 eq.) (3,4-Di(dodecyloxy)phenyl)-tetrazole (**7c**) as well as 0.25 mL DIPEA were dissolved in 10 mL abs. toluene. **Yield:** 311 mg (0.16 mmol; 82 %) yellowish solid. **T_m:** 83 – 100 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.70 (dd, J = 8.4, 2.0 Hz, 4H), 7.65 (d, J = 2.0 Hz, 4H), 6.96 (d, J = 8.6 Hz, 4H), 4.12 – 4.04 (m, 16H), 1.93 – 1.81 (m, 17H), 1.55 – 1.45 (m, 17H), 1.44 – 1.22 (m, 135H), 0.94 – 0.86 (m, 24H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 166.65, 159.20, 153.02, 149.40, 139.07, 121.35, 115.01, 112.79, 111.76, 69.39, 69.14, 31.95, 29.74, 29.72, 29.69, 29.66, 29.65, 29.46, 29.43, 29.40, 29.18, 29.08, 26.05, 26.00, 22.71, 14.14. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2920, 2850, 1603, 1559, 1509, 1499, 1466, 1388, 1270, 1219, 1137, 1076, 1011, 809. **FD-MS:** calculated for C₁₃₂H₂₁₂N₁₀O₁₂: 2129.63, found: 2128.23.

1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (17)

According to general procedure A: 52 mg (0.2 mmol, 1 eq.) of pyrazine tetracarboxylic acid and 389 mg (0.8 mmol, 4 eq.) 5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (**7d**) as well as 0.25 mL DIPEA were dissolved in 10 mL of abs. toluene. **Yield:** 131 mg (0.07 mmol; 34 %) yellowish solid. **T_m:** 93 – 109 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.73 – 7.64 (m, 8H), 6.97 (d, *J* = 8.5 Hz, 4H), 4.17 – 4.06 (m, 16H), 1.98 – 1.87 (m, 8H), 1.77 – 1.49 (m, 40H), 1.41 – 1.31 (m, 26H), 1.24 – 1.12 (m, 30H), 1.0 – 0.94 (m, 27H), 0.91 – 0.86 (m, 62H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 166.67, 159.21, 152.99, 149.40, 139.12, 121.32, 115.00, 112.67, 111.63, 67.72, 67.53, 39.25, 37.38, 37.36, 37.34, 36.10, 35.98, 35.97, 29.96, 29.72, 28.00, 24.74, 22.72, 22.63, 19.71. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2952, 2925, 2869, 1507, 1496, 1472, 1457, 1261, 668. **FD-MS:** calculated for C₁₁₈H₁₈₀N₈O₁₂: 1901.37, found: 1904.03.

1,4-Di(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (18)

According to general procedure A: 51 mg (0.25 mmol, 1 eq.) of terephthalic acid and 243 mg (0.5 mmol, 3 eq.) (3,4-Di(decyloxy)phenyl)-tetrazole (**7b**) as well as 0.13 mL DIPEA were dissolved in 10 mL of abs. toluene. Isolation of target compound via column chromatography. **Yield:** 171 mg (0.17 mmol; 69 %) yellowish solid. **T_m:** ~136 °C (decomposition). **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 8.29 (s, 2H), 7.71 – 7.65 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.10 (dt, *J* = 12.9, 6.6 Hz, 4H), 1.92 – 1.83 (m, 4H), 1.73 – 1.59 (m, 2H), 1.56 – 1.45 (m, 4H), 1.44 – 1.20 (m, 25H), 0.94 – 0.83 (m, 6H). **¹³C NMR (75 MHz, CDCl₃):** δ [ppm] = 165.21, 163.36, 152.53, 149.39, 127.40, 126.61, 120.62, 115.91, 112.87, 111.69, 69.49, 69.16, 31.94, 29.66, 29.64, 29.61, 29.60, 29.45, 29.42, 29.38, 29.22, 29.11, 26.04, 26.01, 22.71, 14.14. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 2918, 2848, 1603, 1509, 1466, 1271, 1220, 1139, 1045, 1014, 987, 856, 808, 723, 668, 657. **FD-MS:** calculated for C₆₂H₉₄N₄O₆: 990.72, found: 990.33.

Pyrazine tetracarboxylic acid (8)[1]

The synthesis was performed according to a procedure reported by Dürr et al. Tetramethylpyrazine (1.5 g, 11 mmol, 1 eq.), sodium carbonate (2.12 g, 20 mmol, 1.82 eq.), and Aliquat 336 (0.53 g, 1.31 mmol, 0.12 eq.) were dissolved in 40 mL of water. Potassium permanganate (23.3 g, 147 mmol, 13.36 eq.) was carefully added over one hour and the reaction mixture was heated to reflux until the potassium permanganate was fully consumed. The reaction mixture was filtered, and the solid residue was extracted with hot water. The combined filtrates were concentrated under reduced pressure and acidified with concentrated HCl. The precipitate (**Potassium-salt** of XX) was filtrated by suction, washed with cold water, and additional solid was recovered by further concentrating and cooling the mother liquor. The combined solids were redissolved in hot water and precipitated using a slight excess of CaCl₂. The resulting precipitate (**Ca-salt** of XX) was filtered by suction, resuspended in cold water, acidified with a small amount of concentrated sulfuric acid, and stirred for one hour. The suspension was filtered, and the solid (CaSO₄) was washed with cold water. The filtrate was concentrated, cooled, and filtered again to obtain pyrazine tetracarboxylic acid as a colorless solid. **Yield:** 1.82g (7.1 mmol; 65 %) colourless solid. **T_m:** 205 – 210 °C (decomposition). **¹³C NMR (75 MHz, D₂O):** δ [ppm] = 167.06, 145.36. **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 3396, 1682, 1618, 1102, 662, 646.

5-(3,4-Di(octyloxy)phenyl)-1H-tetrazol (7a)[2]

According to general procedure B: 5.08 g 3,4-Di(octyloxy)benzonitrile (6a) (14 mmol, 1 eq.) 0.19 g AlCl₃ (1.4 mmol, 0.1 eq.) and 0.91 g NaN₃ (14 mmol, 1 eq.) were suspended in 15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 4.75 g (11.8 mmol; 84 %) beige solid. **T_m:** 164 – 168 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.62 – 7.47 (m, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.03 – 3.93 (m, 1H), 1.77 (m, 1H), 1.50 – 1.15 (m, 20H),

0.89 – 0.77 (m, 6H). **IR (ATR):** ν [cm⁻¹] = 2920, 2850, 1606, 1510, 1464, 1269, 1233, 1135, 1067, 1038, 873, 810, 759, 745, 724, 659.

5-(3,4-Di(decyloxy)phenyl)-1H-tetrazol (7b)[2]

According to general procedure B: 16 g 3,4-Di(decyloxy)benzonitrile (6b) (35 mmol, 1 eq.) 0.46 g AlCl₃ (3.5 mmol, 0.1 eq.) and 2.3 g NaN₃ (35 mmol, 1 eq.) were suspended in 15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 13.76 g (30 mmol; 85 %) beige solid. **T_m:** 158 – 159 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.64 (d, J = 2.0 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.07 – 3.95 (m, 4H), 1.82 (m, 4H), 1.52 – 1.18 (m, 28H), 0.91 – 0.80 (m, 6H).

5-(3,4-Di(dodecyloxy)phenyl)-1H-tetrazol (7c)[2]

According to general procedure B: 3.93 g 3,4-Di(dodecyloxy)benzonitrile (6c) (8.3 mmol, 1 eq.) 0.11 g AlCl₃ (0.8 mmol, 0.1 eq.) and 1.35 g NaN₃ (8.3 mmol, 1 eq.) were suspended in 15 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 13.76 g (30 mmol; 85 %) brown solid. **T_m:** 153 – 157 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.53 (d, J = 2.0 Hz, 1H), 7.49 (dd, J = 8.3, 2.1 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 3.93 (m, 4H), 1.71 (m, 4H), 1.43 – 1.05 (m, 36H), 0.80 – 0.70 (m, 6H). **IR (ATR):** ν [cm⁻¹] = 2920, 2849, 1606, 1510, 1465, 1270, 1235, 1131, 1038, 875, 810, 745, 723, 715, 682, 669.

5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (7d)[2]

According to general procedure B: 3.0 g 3,4-Di((3,7-dimethyloctyl)oxy)benzonitrile (6d) (6.54 mmol, 1 eq.) 0.09 g AlCl₃ (0.65 mmol, 0.1 eq.) and 0.425 g NaN₃ (6.54 mmol, 1 eq.) were suspended in 10 mL NMP. Aqueous work-up and recrystallization from acetonitrile. **Yield:** 2.13 g (4.65 mmol; 65 %) beige solid. **T_m:** 94 – 95 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.71 (d, J = 7.2 Hz, 2H), 7.02 – 6.96 (m, 1H), 4.09 (m, 4H), 1.87 (m, 2H), 1.75 – 1.43 (m, 6H), 1.40 – 1.04 (m, 12H), 0.95 (d, J = 6.3 Hz, 3H), 0.91 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 6.6 Hz, 12H).

3,4-Di(octyloxy)benzonitrile (6a)[2]

According to general procedure A: 2.7 g (20 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 8.3 g (60 mmol, 3 eq.) K₂CO₃ and 7.3 mL (42 mmol, 2.1 eq.) octylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether. **Yield:** 5.1 g (14.2 mmol; 71 %) colorless solid. **T_m:** 73 – 74 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.23 (dd, J = 8.3, 1.9 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 4.06 – 3.99 (m, 4H), 1.88 – 1.77 (m, 4H), 1.51 – 1.22 (m, 20H), 0.91 – 0.86 (m, 6H). **IR (ATR):** ν [cm⁻¹] = 2952, 2917, 2871, 2849, 2219, 1595, 1579, 1517, 1468, 1421, 1395, 1335, 1274, 1243, 1168, 1137 1058, 1012, 997, 984, 957, 943, 914, 855, 836, 810, 805, 753, 736, 722, 695, 653.

3,4-Di(decyloxy)benzonitrile (6b) [2]

According to general procedure A: 3.4 g (25 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 10.4 g (75 mmol, 3 eq.) K₂CO₃ and 11 g (50 mmol, 2 eq.) decylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether. **Yield:** 7.9 g (19 mmol; 76 %) colorless solid. **T_m:** 78 – 79 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.23 (dd, J = 8.4, 1.9 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 4.04 – 3.97 (m, 4H), 1.87 – 1.78 (m, 4H), 1.50 – 1.27 (m, 28H), 0.90 – 0.86 (m, 6H).

3,4-Di(dodecyloxy)benzonitrile (6c) [2]

According to general procedure A: 2.7 g (20 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 8.3 g (60 mmol, 3 eq.) K₂CO₃ and 10.1 mL (42 mmol, 2.1 eq.) dodecylbromide were suspended in 50 mL ACN. Aqueous work-up and recrystallization from petroleum ether.

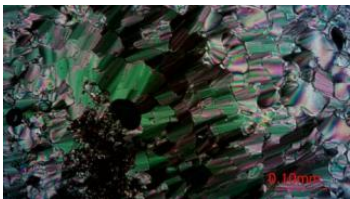
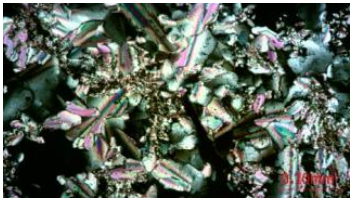
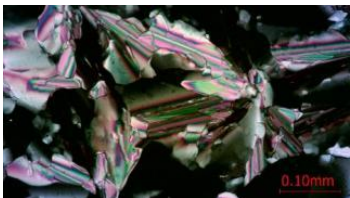
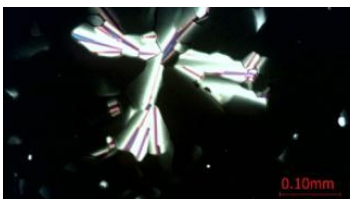
Yield: 3.9 g (19 mmol; 42 %) colorless solid. **T_m:** 83 – 84 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.23 (dd, J = 8.4, 1.9 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 4.04 – 3.97 (m, 4H), 1.87 – 1.78 (m, 4H), 1.50 – 1.27 (m, 28H), 0.90 – 0.86 (m, 6H). **IR (ATR):** ν [cm⁻¹] = 2953, 2915, 2872, 2848, 2220, 1596, 1580, 1519, 1468, 1422, 1396, 1336, 1277, 1242, 1169, 1138, 1069, 1030, 992, 955, 905, 854, 810, 721, 664, 658.

3,4-Di((3,7-dimethyloctyl)oxy)benzonitrile (6d)[2]

According to general procedure A: 1.2 g (9 mmol, 1.0 eq) 3,4-dihydroxybenzonitrile, 5 g (36 mmol, 4 eq.) K₂CO₃ and 5.2 g (20 mmol, 2.1 eq.) 3,7-dimethyloctyl mesylate were suspended in 25 mL ACN. Aqueous work-up and column chromatography. **Yield:** 2.13 g (4.65 mmol; 52 %) beige solid. **T_m:** 94 – 95 °C. **¹H NMR (300 MHz, CDCl₃):** δ [ppm] = 7.71 (d, J = 7.2 Hz, 2H), 7.02 – 6.96 (m, 1H), 4.09 (tt, J = 6.4, 3.1 Hz, 4H), 1.87 (h, J = 7.4 Hz, 2H), 1.75 – 1.43 (m, 6H), 1.40 – 1.04 (m, 12H), 0.95 (d, J = 6.3 Hz, 3H), 0.91 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 6.6 Hz, 12H).

Textures POM

Table S1: Textures

Compound	Texture		T / °C	Texture
TOBE ₈			155	mosaic texture
TOBE ₁₀			155	Pseudo focal conic fans
TOBE ₁₂			150	Mosaic texture
TOBE _{8,1,1}			120	Pseudo focal conic fans
TOPY ₈			185	Pseudo focal conic fans
TOPY ₁₀			180	Pseudo focal conic fans
TOPY ₁₂			170	Pseudo focal conic fans
TOPY _{8,1,1}			102	Mosaic texture

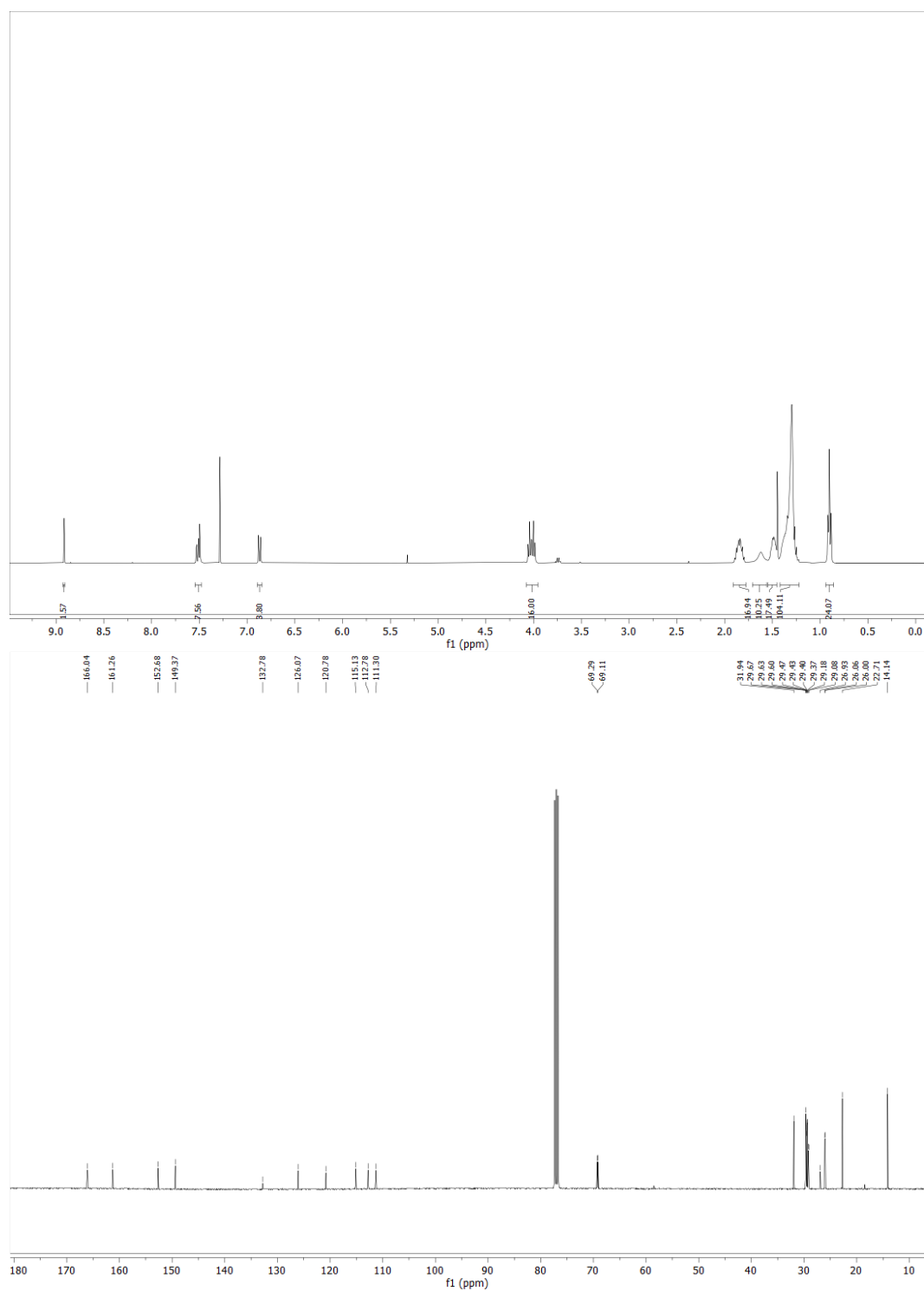


Figure S2. 1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11) in CDCl₃.

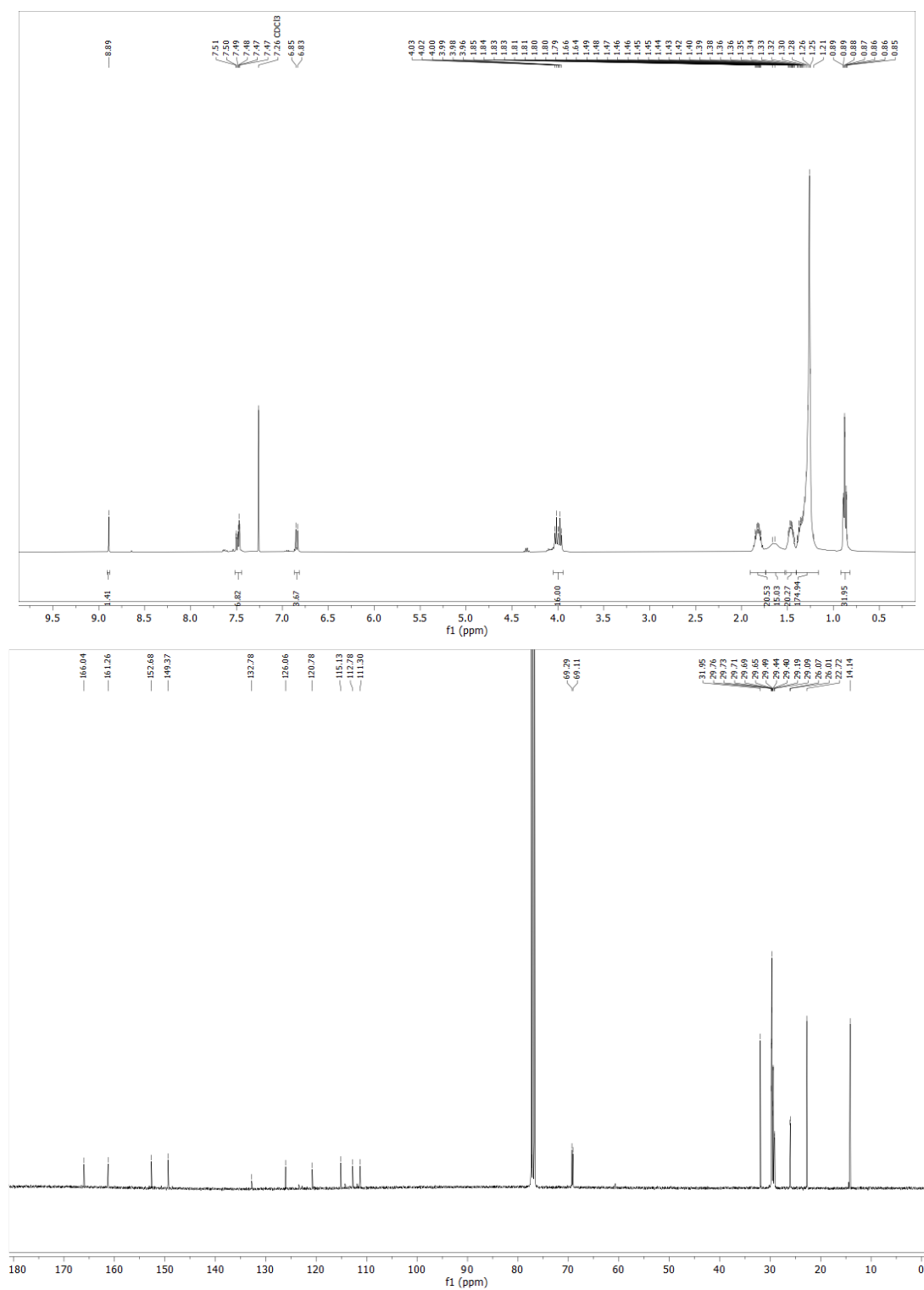


Figure S3. 1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (12) in CDCl₃.

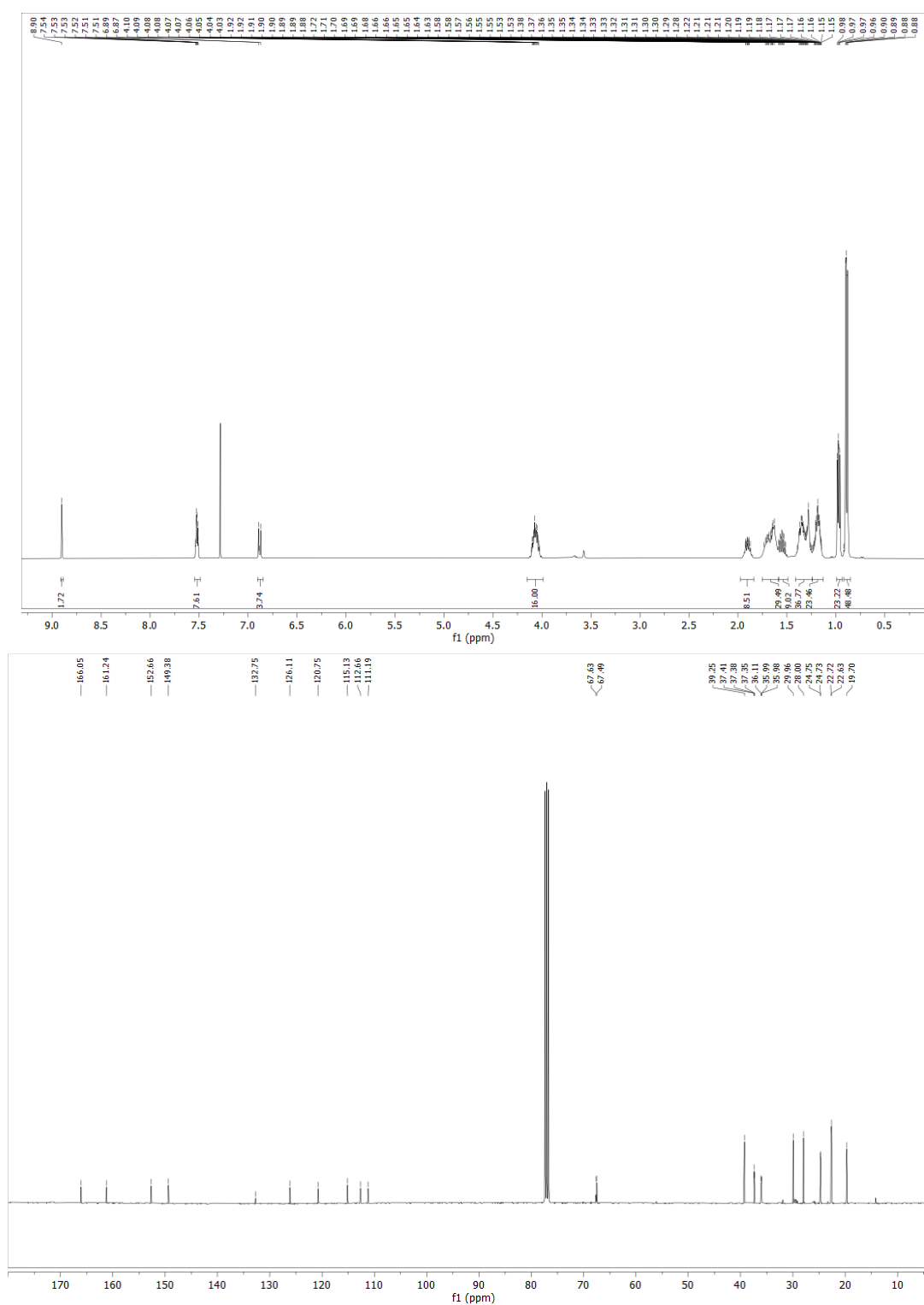


Figure S4. 1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (13) in CDCl_3 .

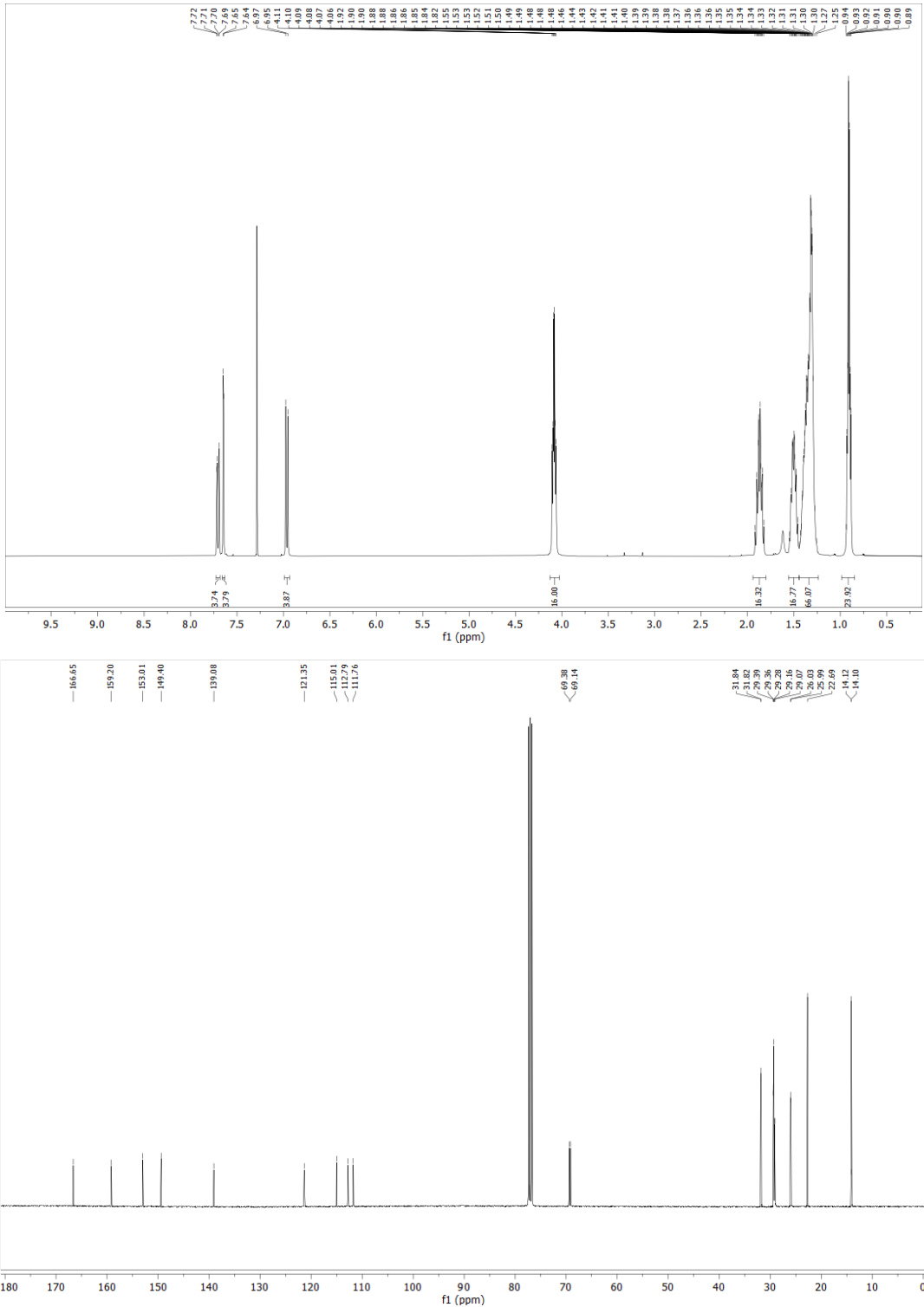


Figure S5. 2,3,5,6-Tetrakis(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (14) in CDCl₃.

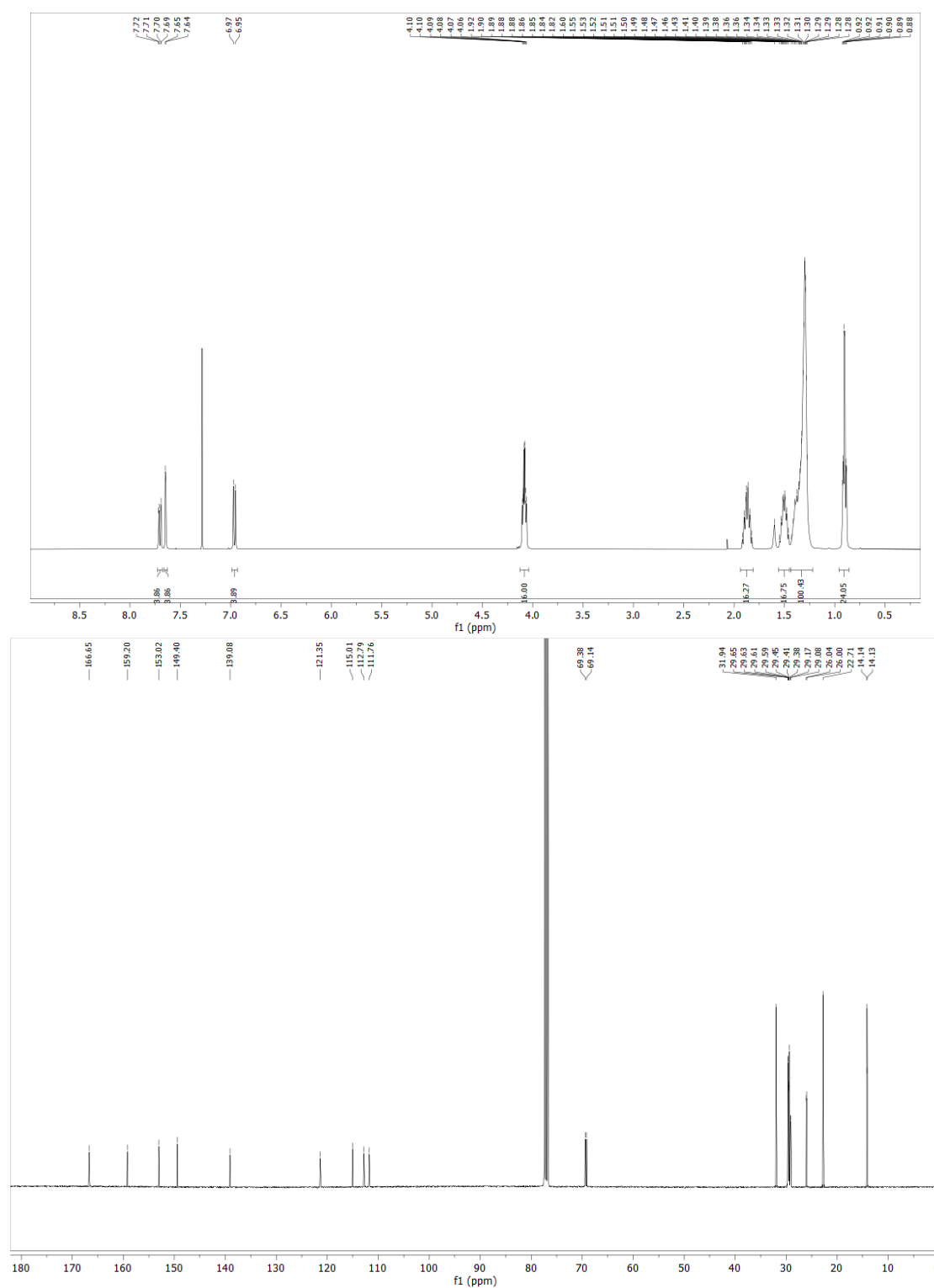


Figure S6. 1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (15) in CDCl₃.

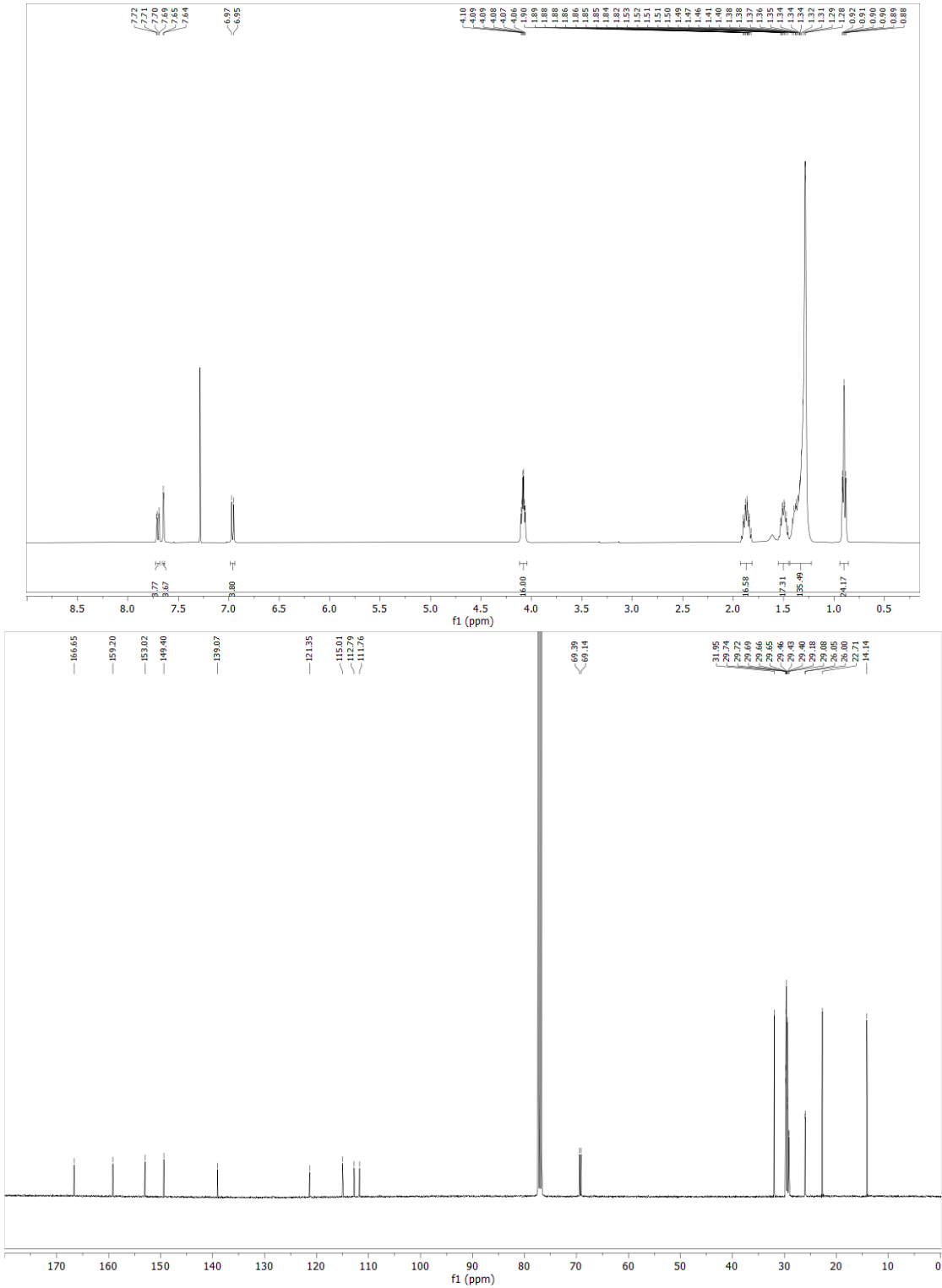


Figure S7. 1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (16) in CDCl₃.

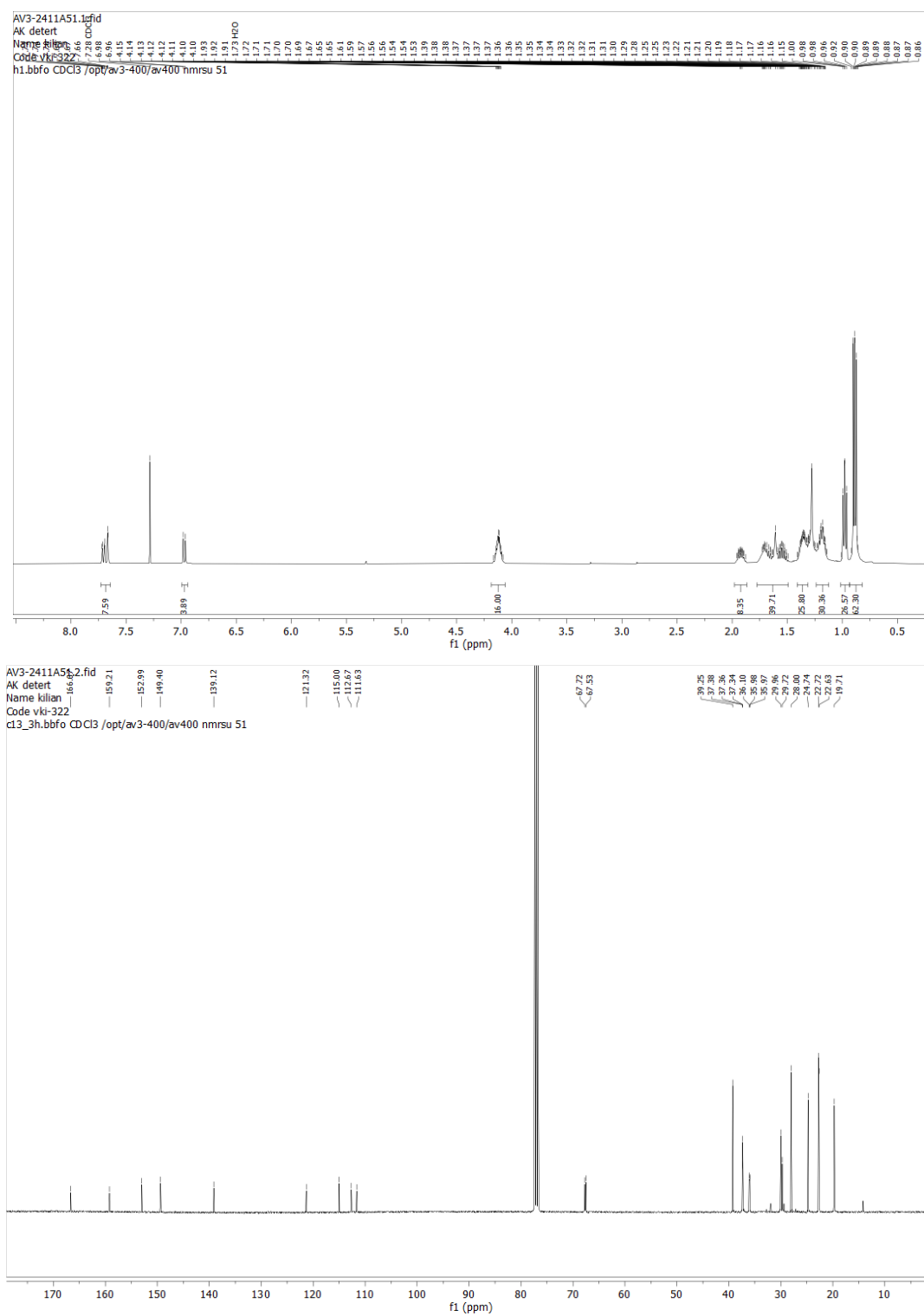


Figure S8. 1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (17) in CDCl₃.

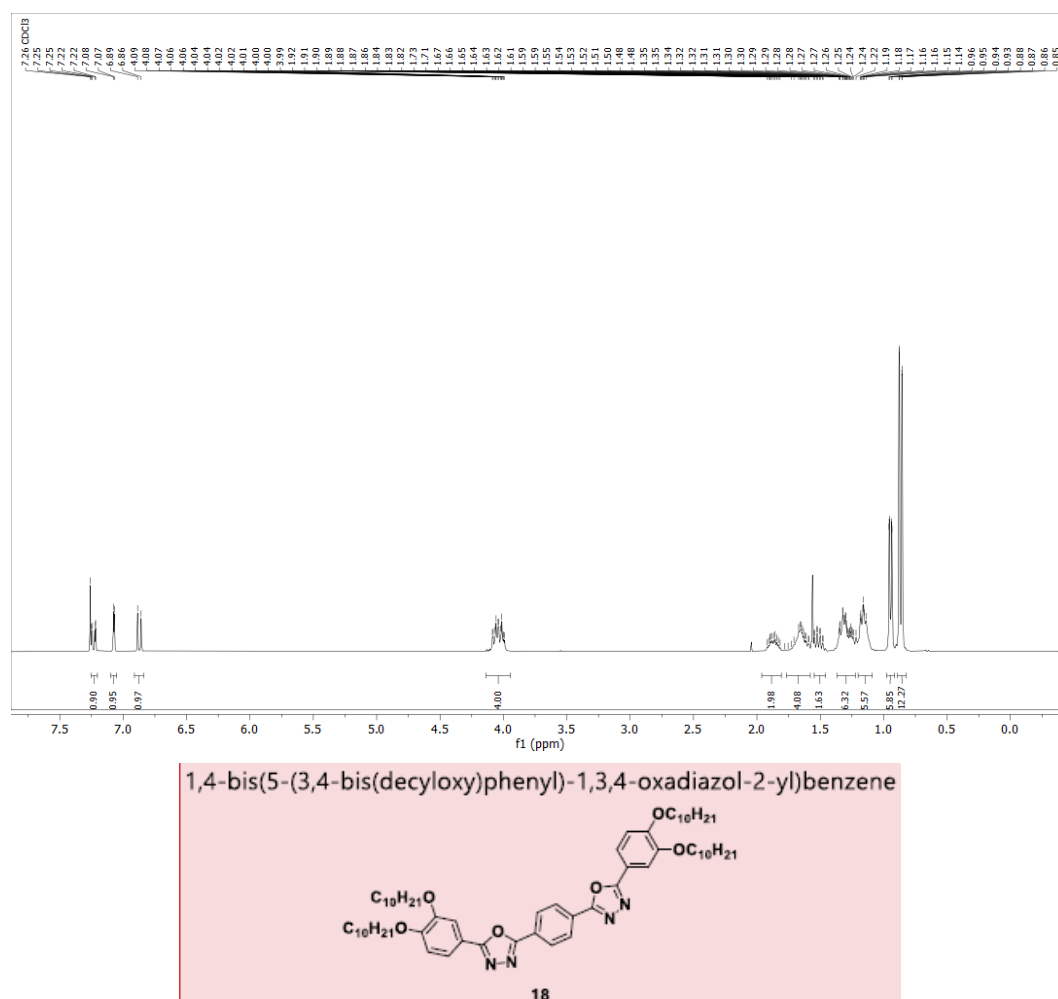


Figure S9. 1,4-Bis(2-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (19) in CDCl_3 .

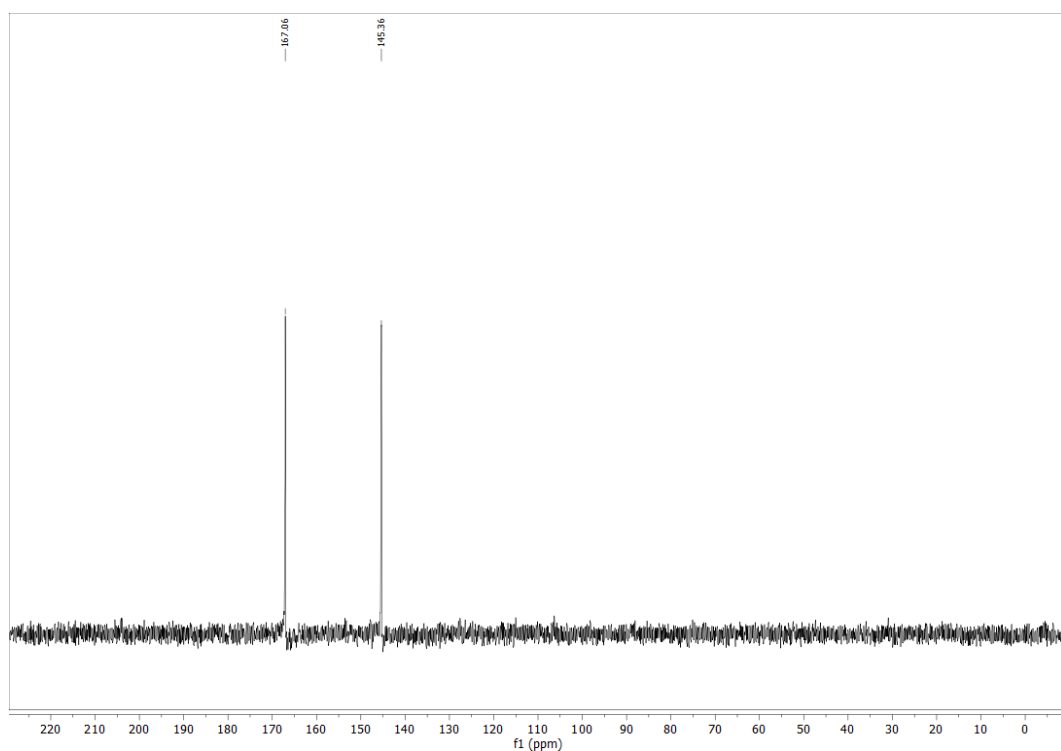


Figure S10. Pyrazine tetracarboxylic acid (8).

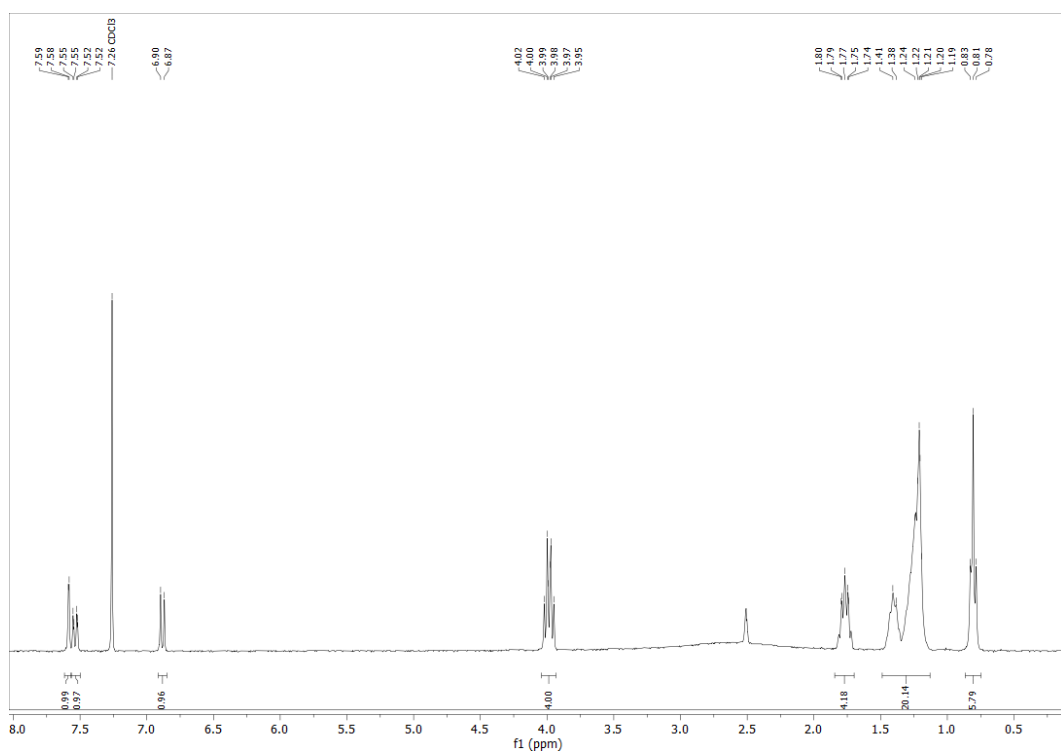


Figure S11. 5-(3,4-Di(octyloxy)phenyl)-1H-tetrazol (7a) in $\text{CDCl}_3/\text{DMSO-d}_6$ (50/1).

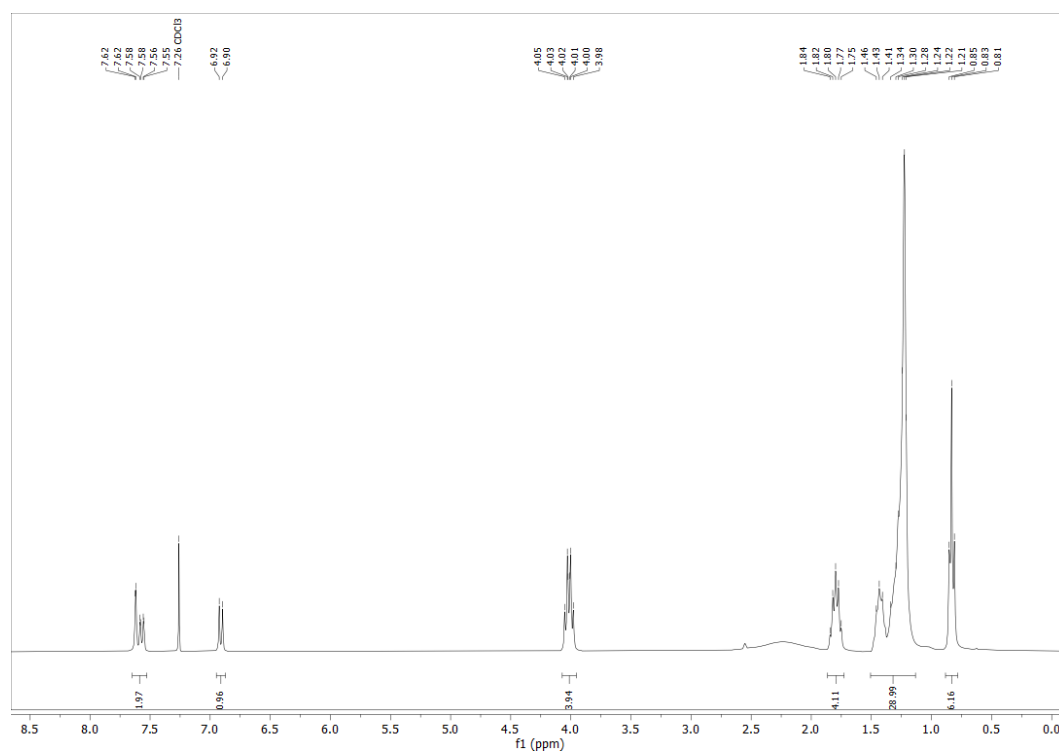


Figure S12. 5-(3,4-Di(decyloxy)phenyl)-1H-tetrazol (7b) in CDCl₃/DMSO-d₆ (50/1).

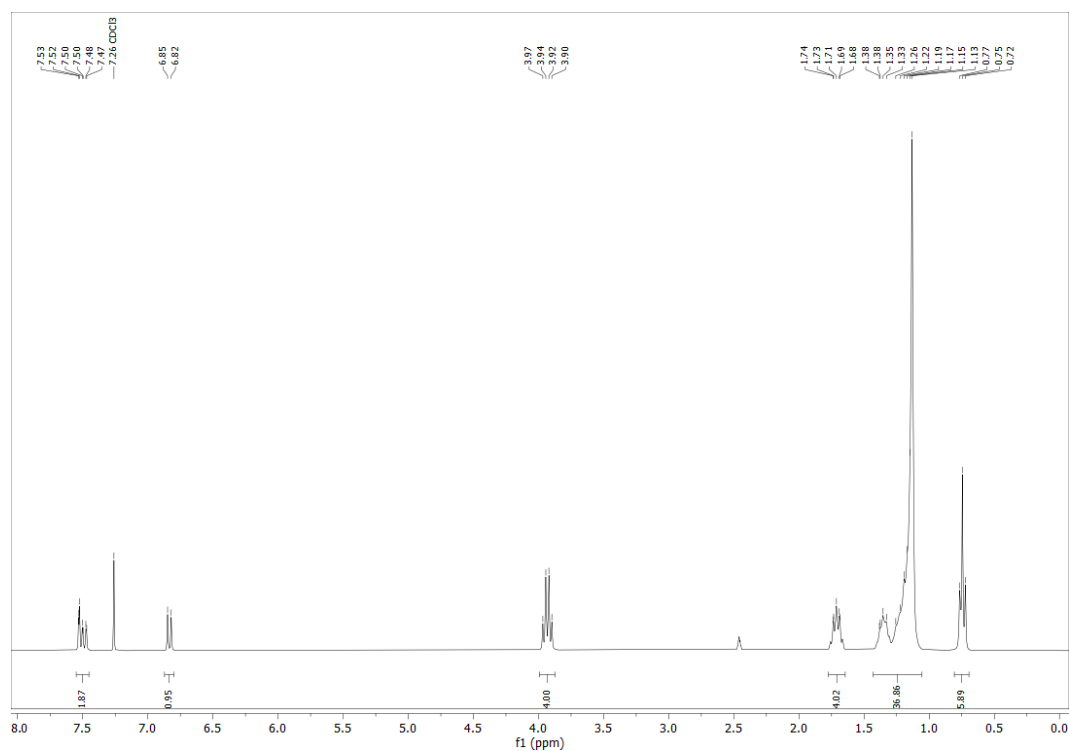


Figure S13. 5-(3,4-Di(dodecyloxy)phenyl)-1H-tetrazol (7c) in CDCl₃/DMSO-d₆ (50/1).

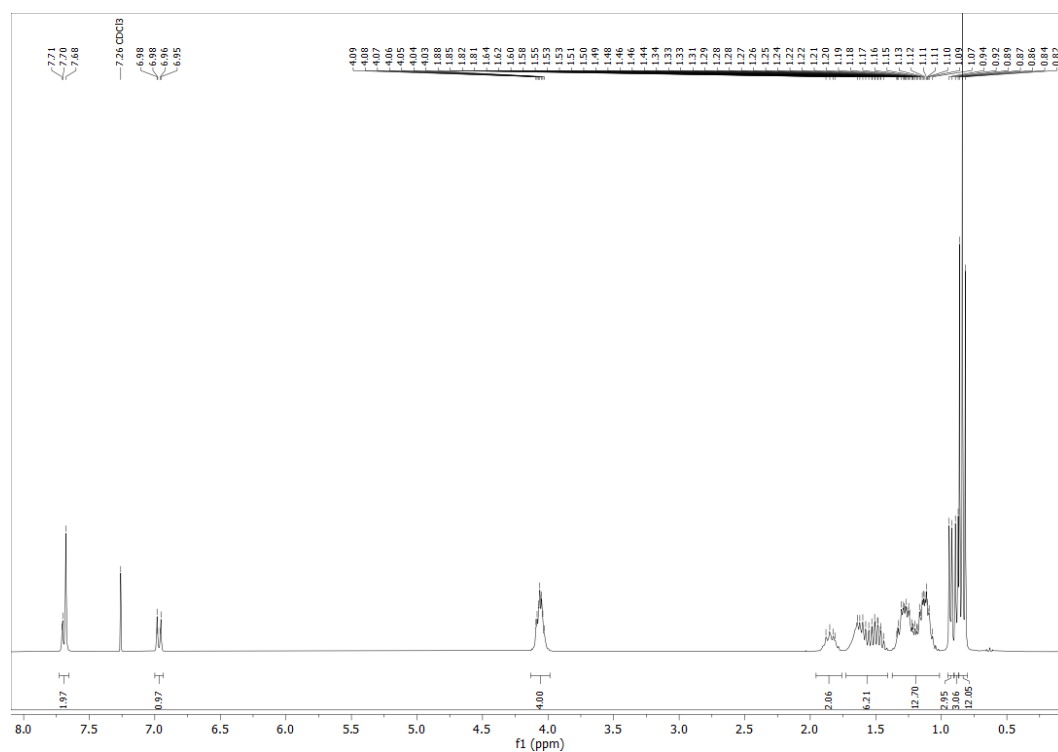


Figure S14. 5-(3,4-Di((3,7-dimethyloctyl)oxy)phenyl)-1H-tetrazole (7d) in CDCl₃.

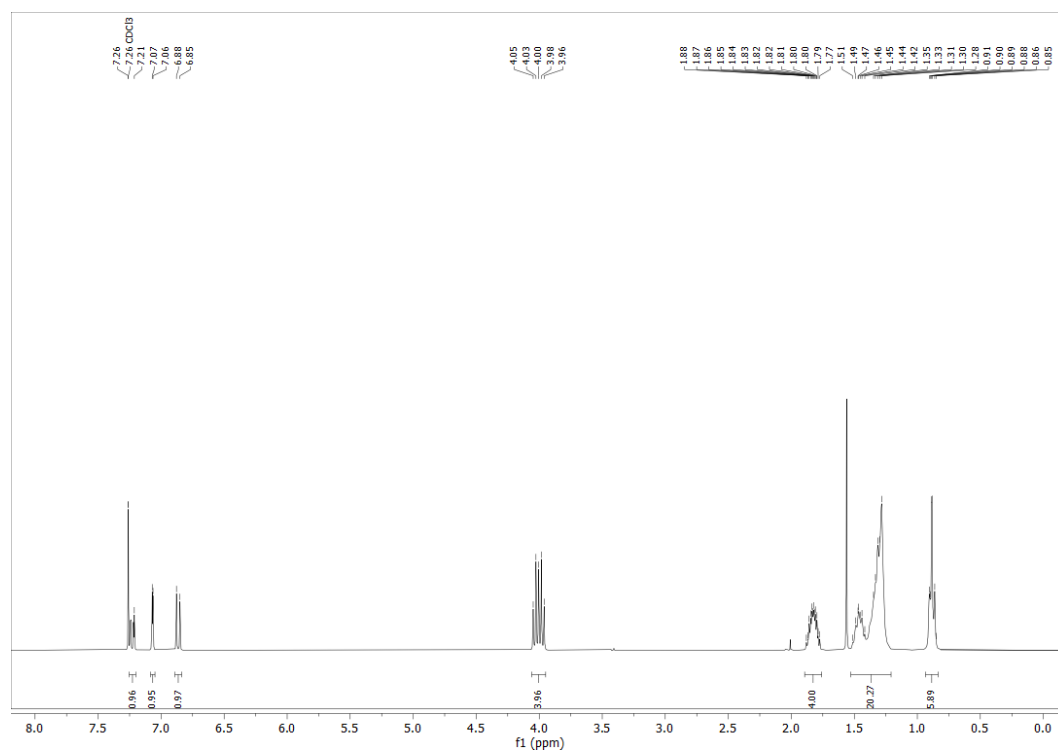


Figure S15. 3,4-Di(octyloxy)benzonitrile (6a) in CDCl₃.

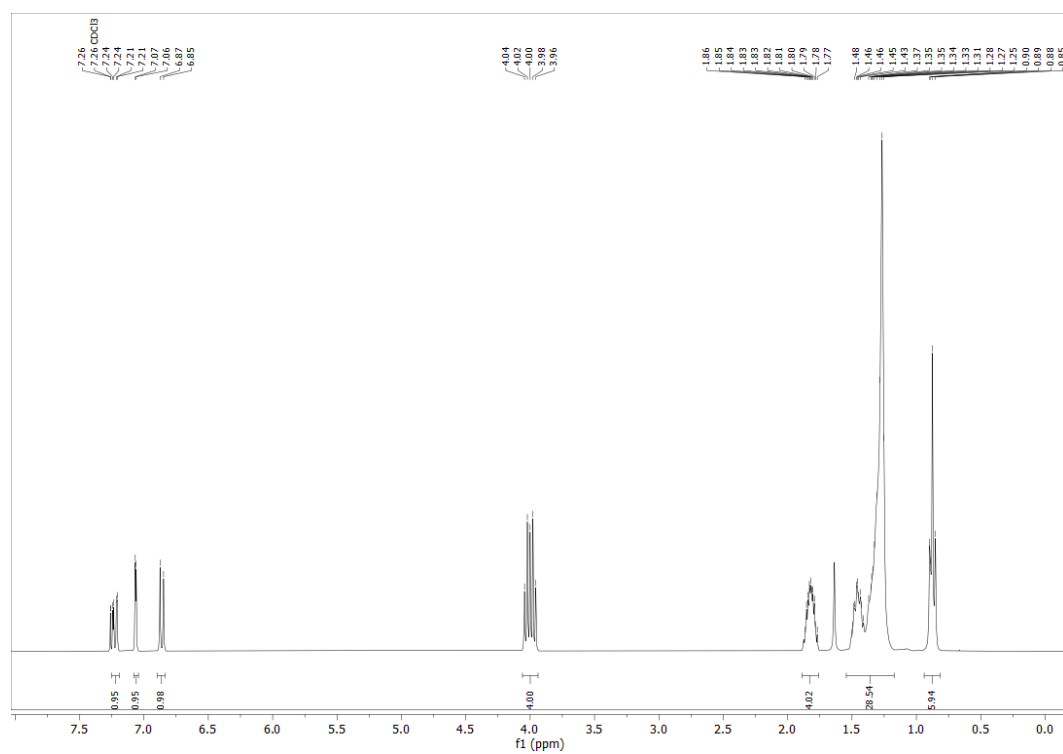


Figure S16. 3,4-Di(decyloxy)benzonitrile (6b) in CDCl₃.

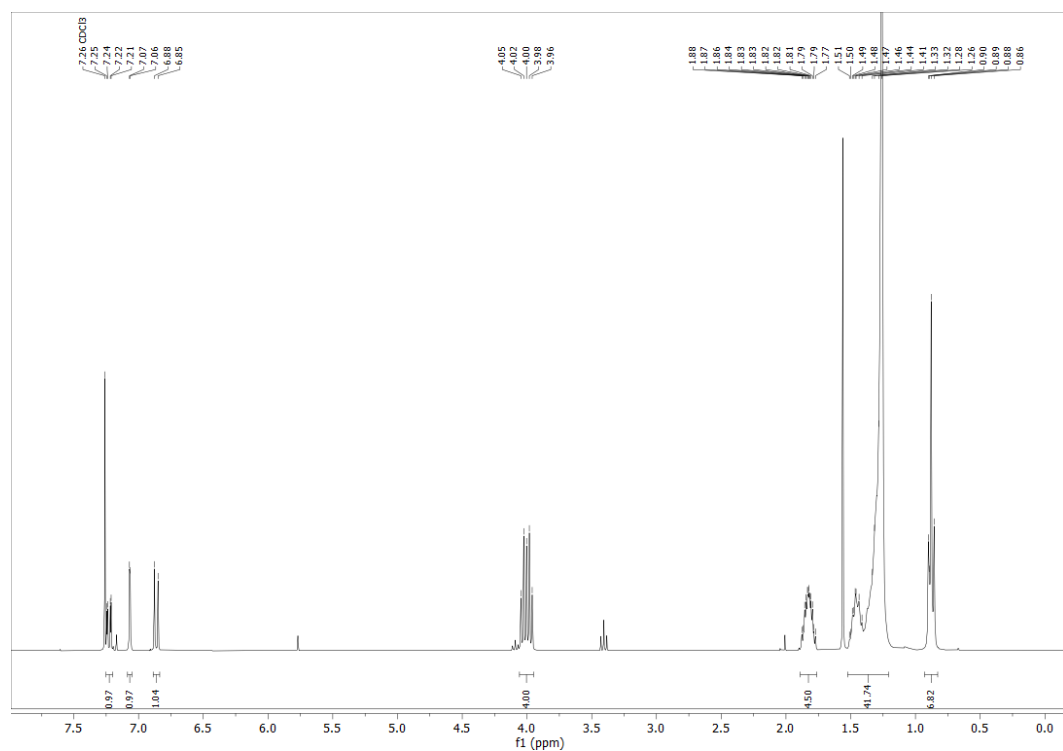


Figure S17. 3,4-Di(dodecyloxy)benzonitrile (6c) in CDCl₃.

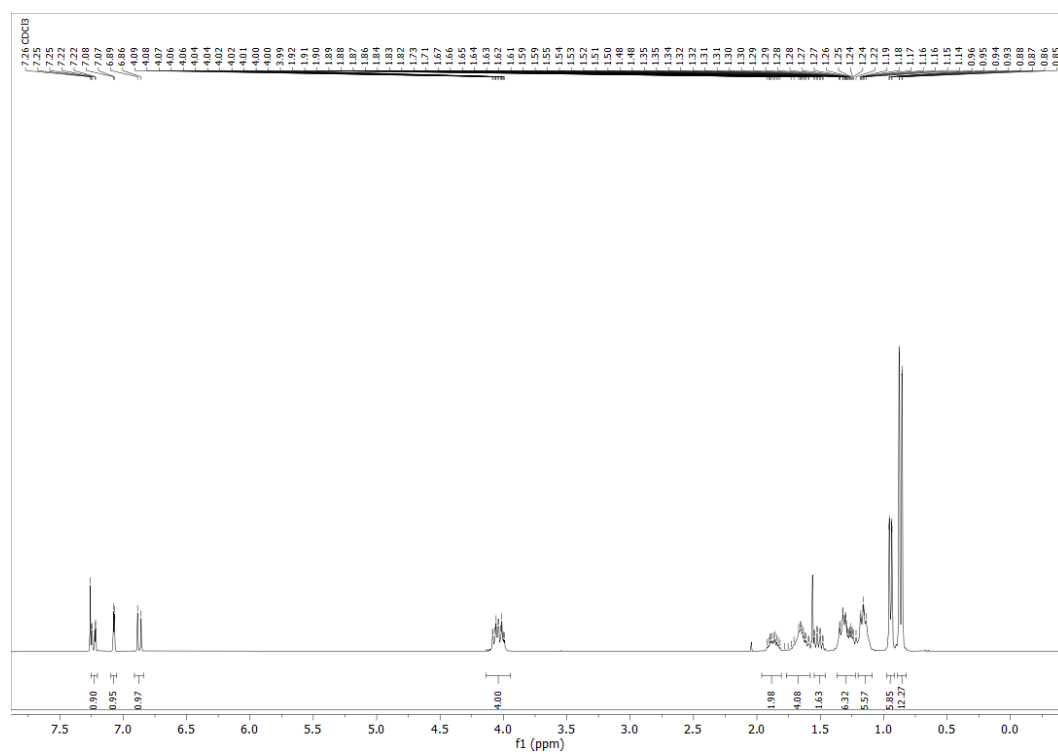


Figure S18. 3,4-Di((3,7-dimethyloctyl)oxy)benzonitrile (6d) in CDCl₃.

Phase Transition Temperatures and Enthalpies

Table S2. Phase Transition Temperatures and Enthalpies of TOBE, TOPY, TOPPS, TOBs and TOTs. Temperature values are given as onset signals of second heating curve.

Compound	T _m * [°C]	ΔH [kJ/mol]	TC* [°C]	ΔH [kJ/mol]
TOBE ₈	146.9	17.9	160.3	7.1
TOBE ₁₀	136.2	25.9	158.3	8.0
TOBE ₁₂	130.9	72.0	183.6	0.9
TOBE _{8,1,1}	98	28.9	123.2	7.6
TOPY ₈	108.1	43.4	189.9	10.3
TOPY ₁₀	99.8	33.4	188.0	9.2
TOPY ₁₂	91.5	35.4	176.3	9.6
TOPY _{8,1,1}	97.6	16.0	/	/
TOB ₁₀	107	26.7	176.0	18.4
TOT ₁₀	84	3.9	203	4.3
TOPP ₁₀	76	3	196	9

*onset signals of second heating curve

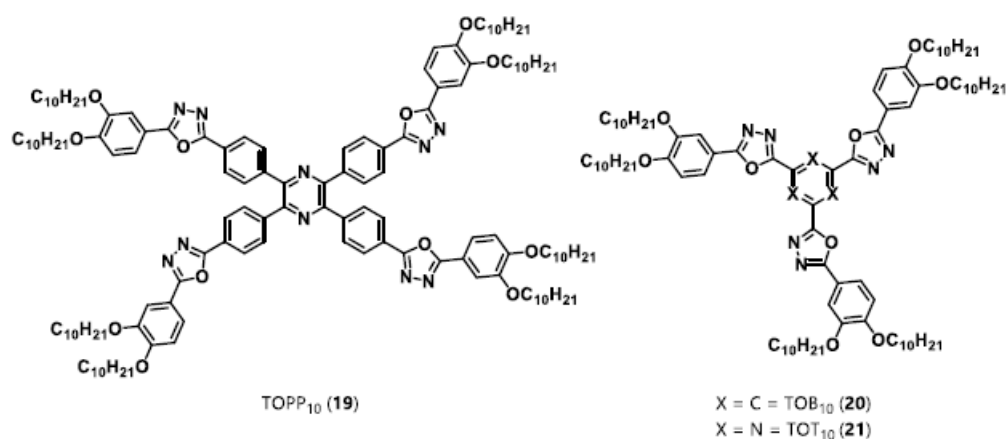


Figure S19. Structures of cruciform and star-like mesogens previously reported by our group [3,4].

DSC-Curves

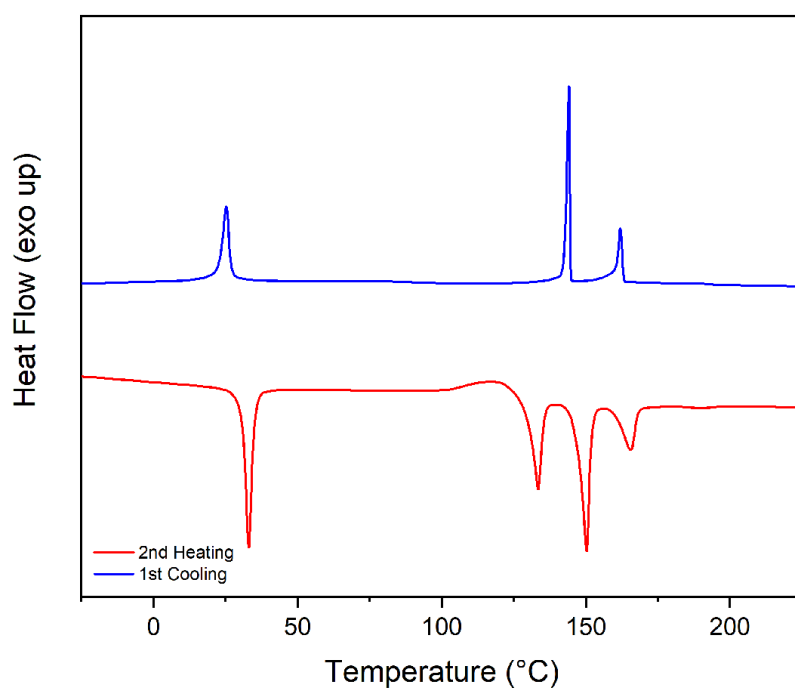


Figure S20. 1,2,4,5-Tetrakis(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (10).

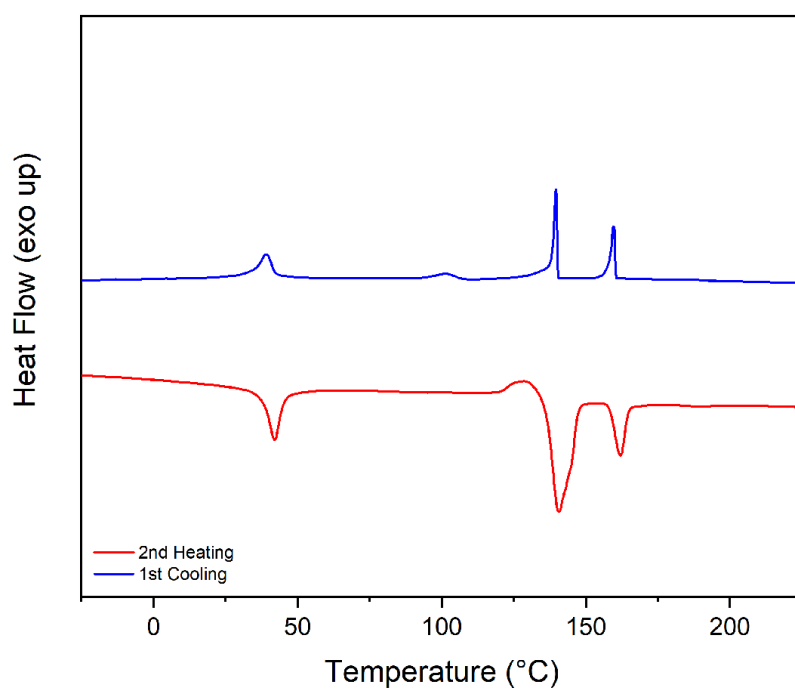


Figure S21. 1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (11).

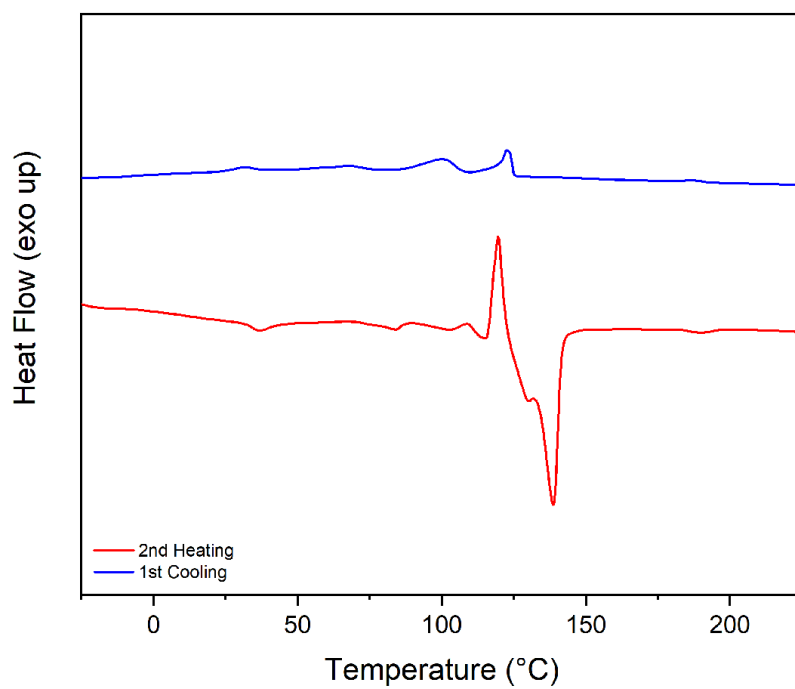


Figure S22. 1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (12).

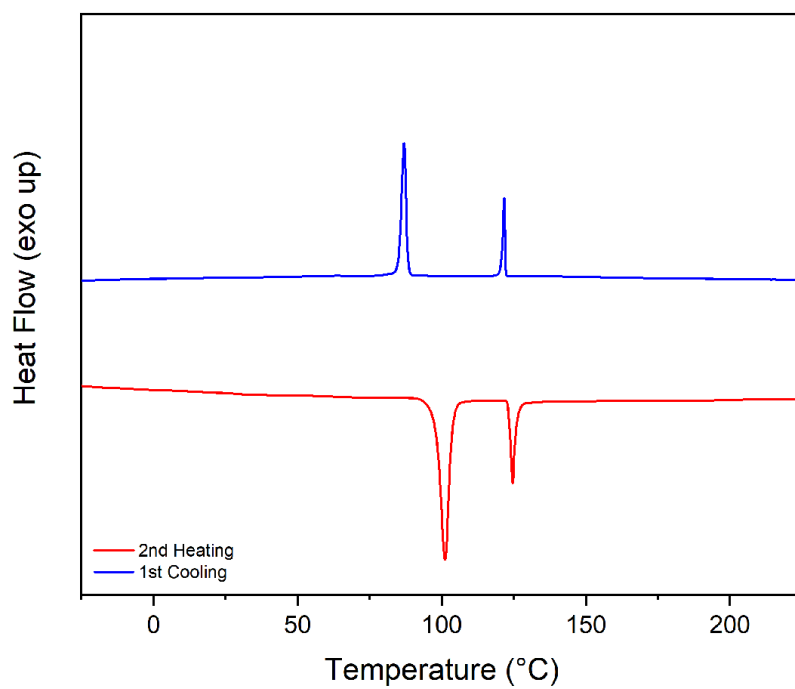


Figure S23. 1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)benzene (13).

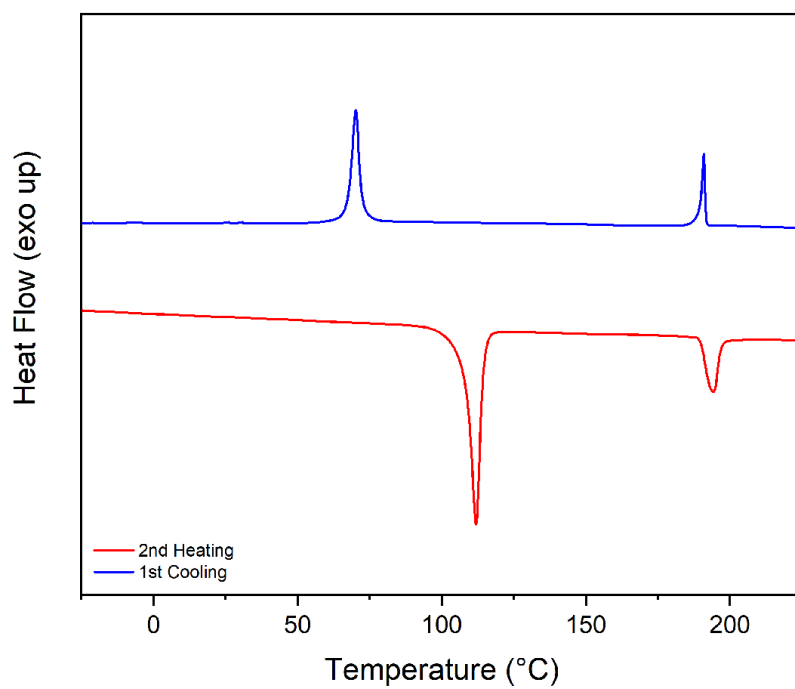


Figure S24. 2,3,5,6-Tetrakis(5-(3,4-bis(octyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (14).

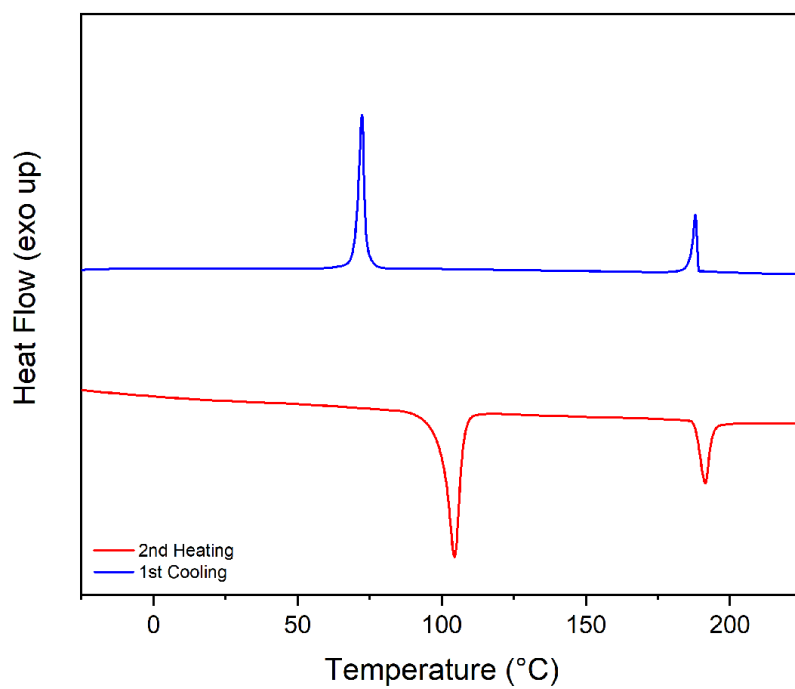


Figure S25. 1,2,4,5-Tetrakis(5-(3,4-bis(decyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (15).

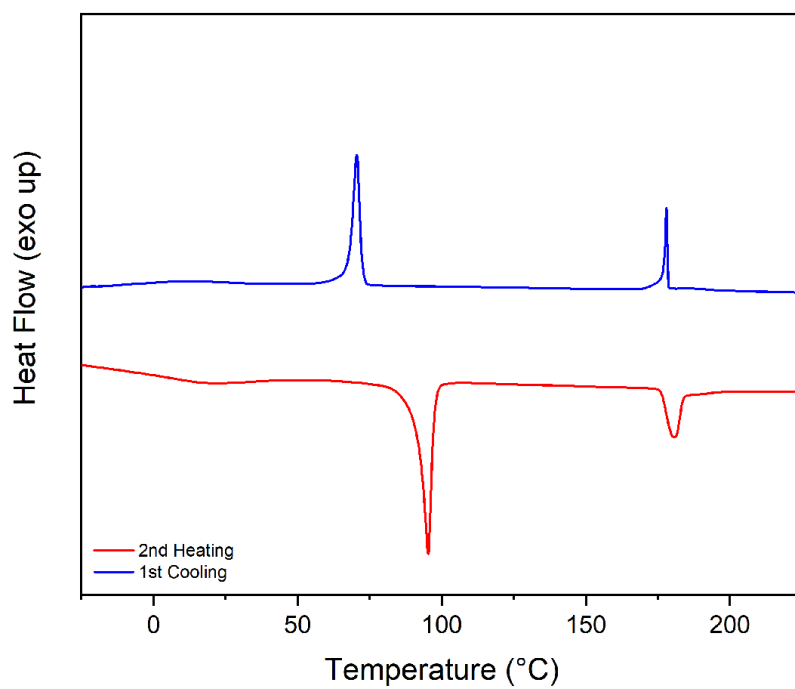


Figure S26. 1,2,4,5-Tetrakis(5-(3,4-bis(dodecyloxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (16).

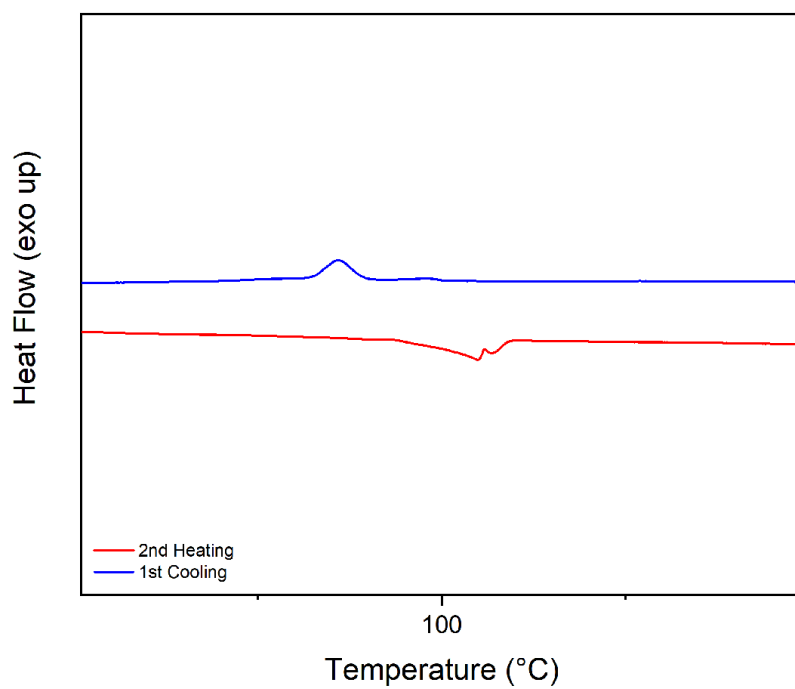


Figure S27. 1,2,4,5-Tetrakis(5-(3,4-bis((3,7-dimethyloctyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)pyrazine (17).

UV-Vis and Fluorescence Spectroscopy

Table S3. UV-Vis- and Fluorescence Spectroscopy in solution of 11, 13, 15.

Compound	Solvent	$\lambda_{\text{max abs}}$ [nm]	ϵ [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]	$\lambda_{\text{max Fl}}$ [nm]	$\Delta\bar{\nu}^{\text{st}}$ [cm^{-1}]	ΦF [%]
TOBE ₁₀ (11)	cyclohexane	365	$5.76 \cdot 10^4$	442	4747	42
	toluene	363	$5.46 \cdot 10^4$	470	6249	72
	dichloro- methane	362	$4.86 \cdot 10^4$	508	7939	28
TOPY ₁₀ (15)	cyclohexane	388	$5.62 \cdot 10^4$	472	4564	13
	toluene	395	$4.98 \cdot 10^4$	512	5766	21
	dichloro- methane	391	$4.96 \cdot 10^4$	570	8016	1
TOBE _{8.1.1} (13)	dichloro- methane	363	$4.86 \cdot 10^4$	513	8074	27

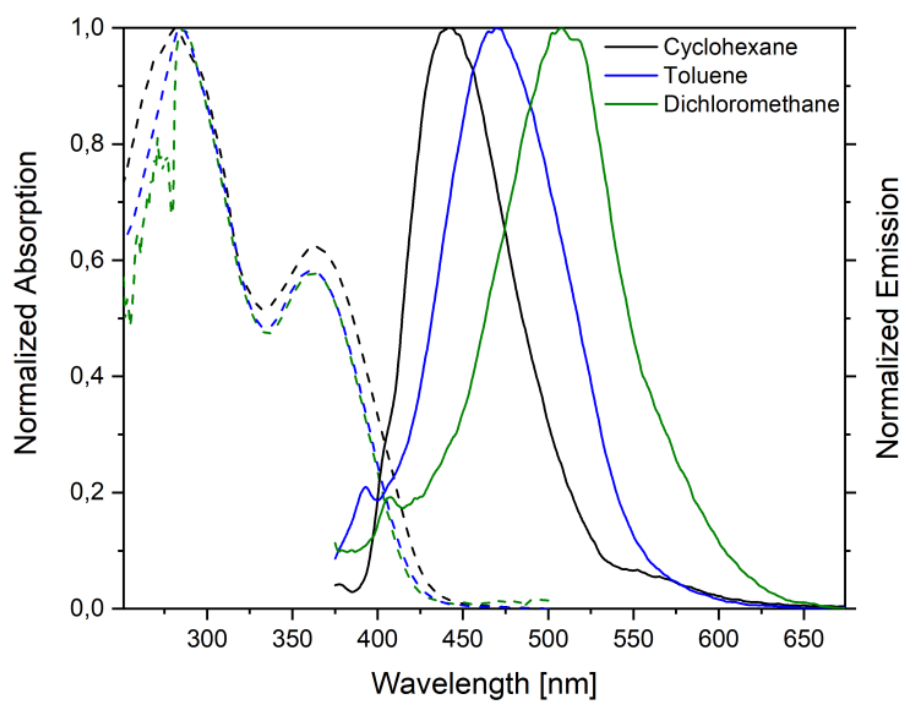


Figure S28. Spectroscopic data of 11 in various solvents. Normalized absorption (dashed), normalized emission (solid).

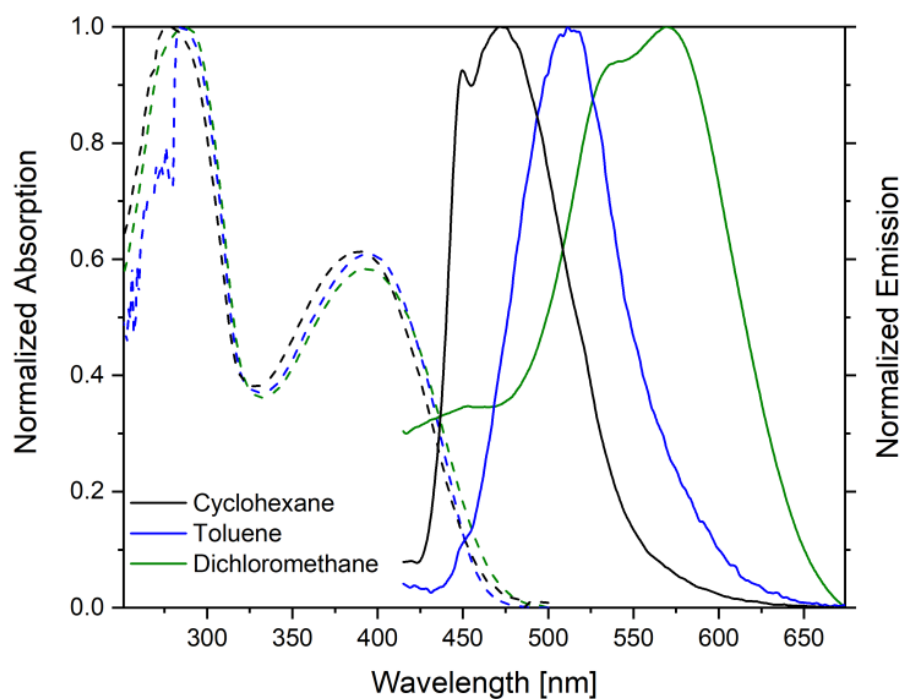


Figure S29. Spectroscopic data of 14 in various solvents. Normalized absorption (dashed), normalized emission (solid).

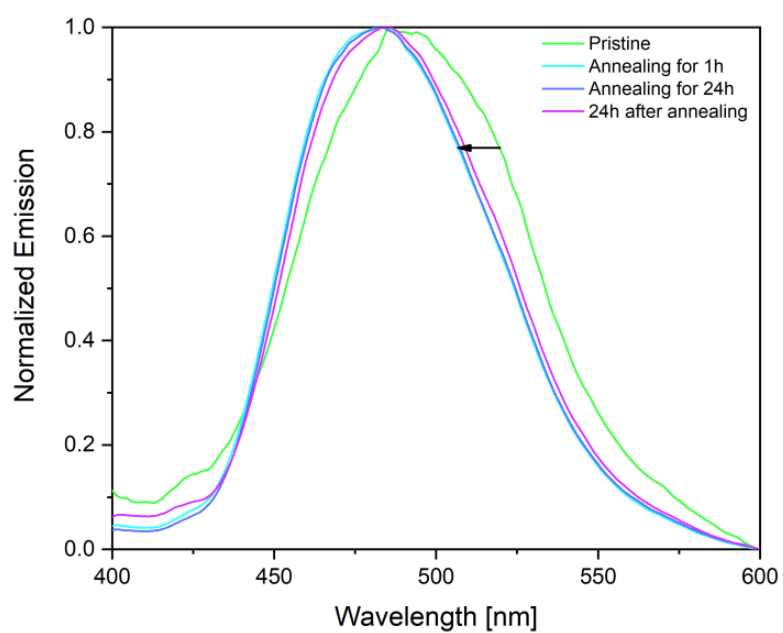


Figure S30. Annealing experiment of spin-coated film of 11. Hypsochromic shift indicated by arrow.

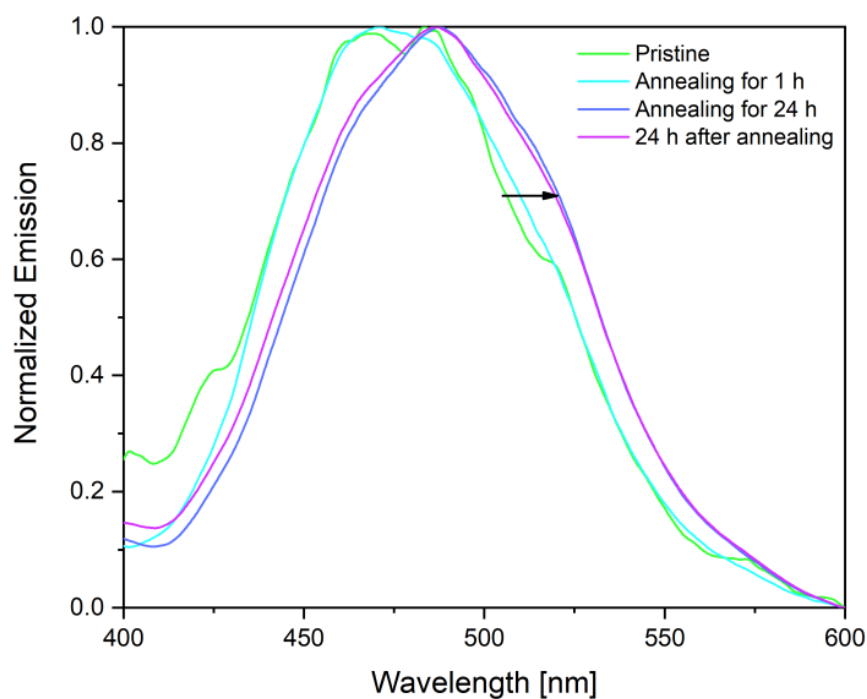


Figure S31. Annealing experiment of spin-coated film of 13. Bathochromic shift indicated by arrow.

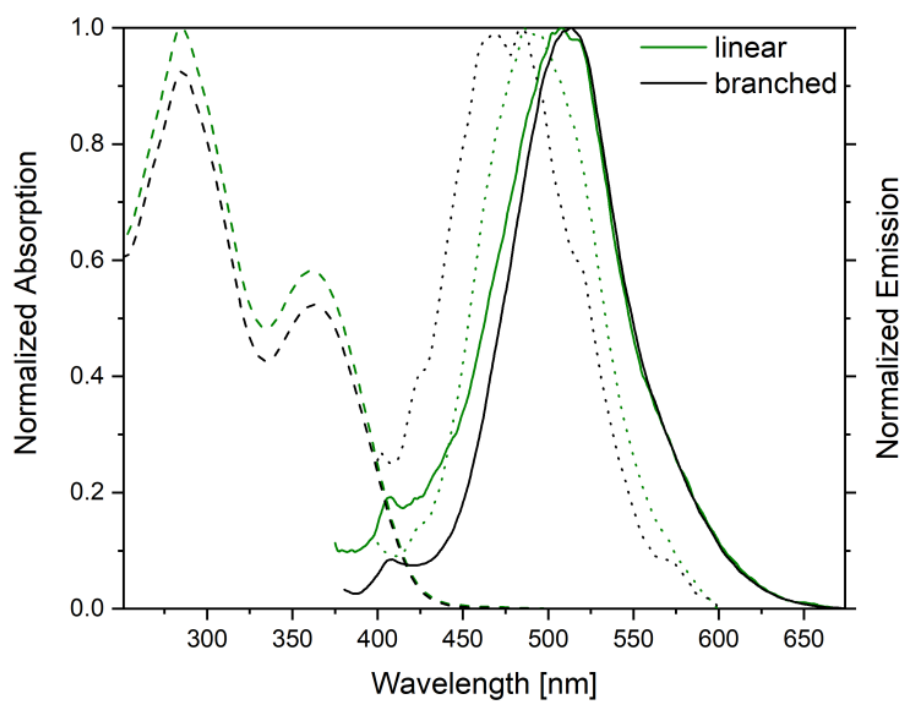


Figure S32. Comparison of spectroscopic properties of 11 and 13. Normalized Absorption in DCM (dashed), normalized emission in DCM (solid), normalized emission spin coated film (dotted).

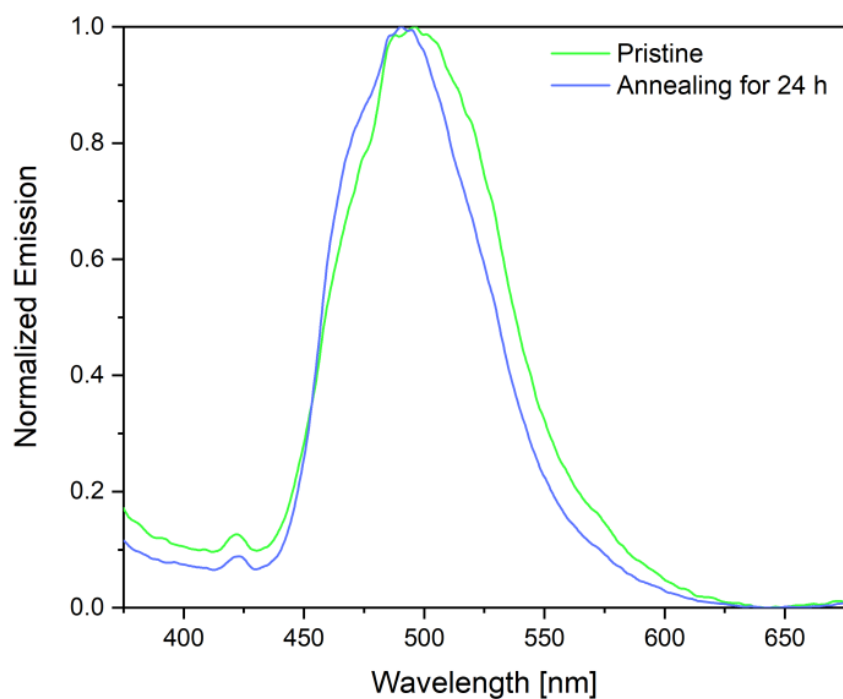


Figure S33. Annealing experiment for spin coated film of 13.

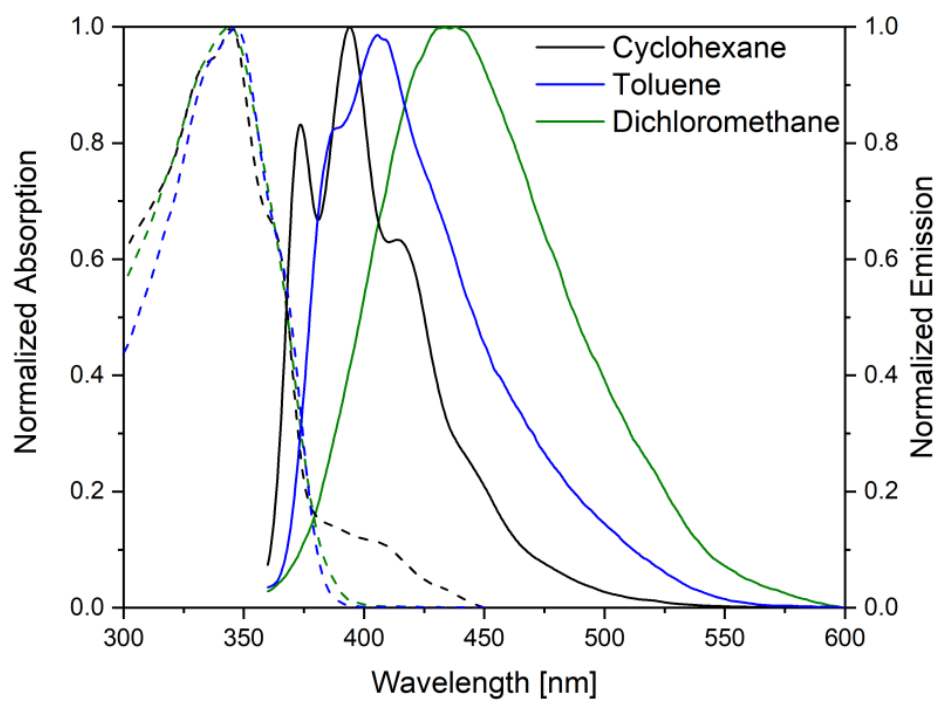


Figure S34. Absorption (dashed) and fluorescence spectra (solid) of compound 18 in various solvents.

2D-Scattering on oriented fiber

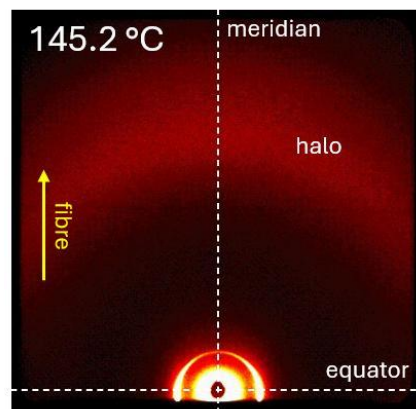
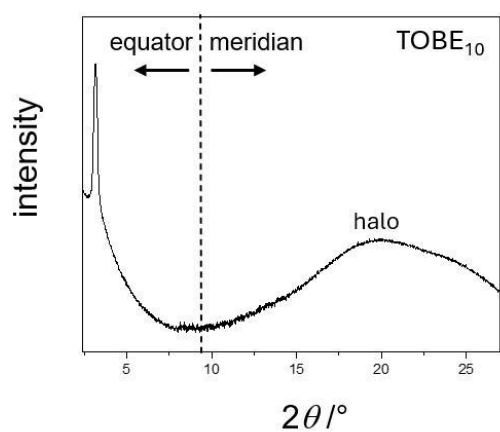
TOBE₁₀ (145.2 °C):

$$a_h = 32.4 \text{ \AA} \quad d_{\text{halo}} = 4.6 \text{ \AA}$$

TOPY₁₀ (124.4 °C):

$$a_h = 32.8 \text{ \AA} \quad d_{\text{halo}} = 4.6 \text{ \AA}$$

A



B

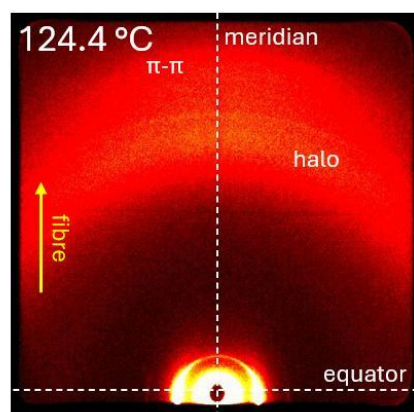
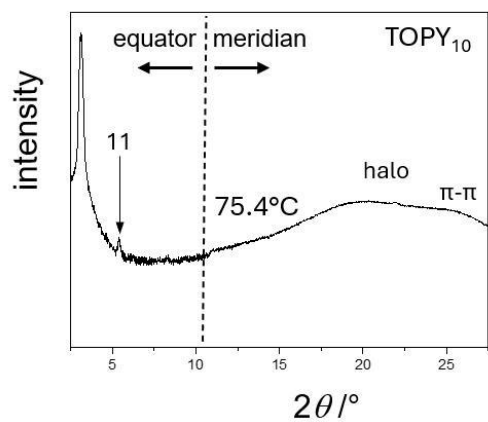


Figure S35. Diffraction pattern and integration along the equator/meridian for 11 (**A**) and 13 (**B**).

References

- [1] Dürr, M.; Klein, J.; Kahnt, A.; Becker, S.; Puchta, R.; Sarkar, B.; Ivanović-Burmazović, I. Redox behavior of a dinuclear ruthenium (II) complex bearing an uncommon bridging ligand: Insights from high-pressure electrochemistry. *Inorg. Chem.* **2017**, *56*, 14912–14925.
- [2] Rieth, T.; Tober, N.; Limbach, D.; Haspel, T.; Sperner, M.; Schupp, N.; Wicker, P.; Glang, S.; Lehmann, M.; Detert, H. Impact of substitution pattern and chain length on the thermotropic properties of alkoxy-substituted triphenyl-tristriazolotriazines. *Molecules* **2020**, *25*, 5761.
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