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Supporting Information to

"Click Chemistry" as a versatile route to synthesize and modulate bent-core liquid crystalline materials

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1. General Information

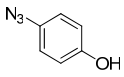
NMR experiments were performed on Bruker Avance 500 and 400 Ultrashield spectrometers. IR spectra were recorded on a BrukerTensor 27 /Diamond ATR and are reported in wavenumbers (cm-1). High-resolution mass spectra were measured on a Waters LCT Premier instrument operated in ESI mode. The textures of the mesophases were studied with an optical microscope (Olympus BH2) with crossed polarizers and connected to a Linkam THS60 hot stage. Photomicrographs were taken with an Olympus DP-12 camera. Measurements of the transition temperatures were made on a TA-MDSC Instruments 2910 and Q-1000 differential scanning calorimeters with a heating or cooling rate of 10°C/min. The apparatus were calibrated with indium (156.6 °C, 28.7 J/g) and tin (232.1 °C, 60.5 J/g). The X-ray studies were carried out using a powder diffractometer equipped with a commercial high temperature attachment (STOE STADI P 0.65.1) that was specifically modified to allow high-resolution measurements at small angles. This device allows a detailed programming of the sample temperature. This was essential in some cases where coexistence of different phases, with a clear dependence of the thermal history, was observed. Measurements were performed in Debye–Scherrer geometry mode using Lindemann capillaries of diameter 0.6 mm. The materials were introduced by capillarity in the isotropic phase. A linear position-sensitive detector, with an angular resolution better than 0.01º, was employed to detect the diffracted intensity in the 2θ interval 0.5-25º (θ is the Bragg angle). A small-angle goniometer with a different temperature controller and a linear position-sensitive detector (PSD) of 4° of angular range was also employed for some of the materials. Monochromatic CuKα1 radiation (λ = 1.5406 Å) was used in all the cases.

2. Synthesis

The synthetic routes followed to prepare the different compounds are shown in Schemes of the main text. Syntheses of compounds **5-8** were described in previous papers.[1] Unless otherwise indicated, all materials were purchased from Aldrich, Fluka and Across. Dry solvents were obtained from an SPS system. All flash

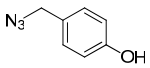
chromatography purifications were carried out using 60 mesh silica gel and dry-packed columns.

Synthesis of 4-azidophenol (1).



4-aminophenol (4.0 g, 36.7 mmol) was suspended in water (100 mL). Concentrated HCl (9 mL) was then added dropwise. After that, the reaction mixture was cooled down to 0 ºC and a solution of $NaNO_2$ (5.1 g, 73.3 mmol) in water (10 mL) was added. The reaction mixture was then stirred for 40 min. at 0 ºC and a solution of sodium azide (2.9 g, 44 mmol) in water (30 mL) was added portionwise. The mixture was allowed to reach rt while stirring for 1 h, and worked up by dilution with ethyl acetate. The organic layer was washed with water (x1) and brine (x1) and dried over sodium sulfate. Compound **1** was obtained as a dark reddish oil and stored at -20 ºC. ^{1}H-NMR (400 MHz, CD_3OD): δ 6.88 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, MeOD) δ 156.59, 133.01, 121.68, 118.26. IR (ATR): ν = 3356, 2106, 2071, 1701, 1504, 1218 cm^{-1}.

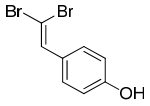
Synthesis of 4-(azidomethyl)phenol (2).



This product was prepared from 4-(hydroxymethyl)phenol (1.24 g, 10.0 mmol), sodium azide (0.78 g, 12.0 mmol), tetrachloromethane (5 mL, 51.8 mmol)and triphenylphosphine (2.62 g, 10.0 mmol) following a reported procedure.[2] A colourless oil was obtained (1.05 g, 71 %). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.26 (brs, 1H), 4.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.96, 129.90, 127.14, 115.65, 54.36. IR (ATR): ν = 3330, 2091, 1611, 1596, 1229, 1170 cm^{-1}.

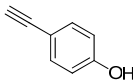
Synthesis of 4-ethynylphenol (3).

i) Synthesis of 4-(2,2-dibromovinyl)phenol:



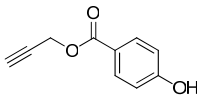
To a ice-bath cooled solution of carbon tetrabromide (10.86 g, 32.8 mmol) in dry dichloromethane (20 mL, SPS quality) inside a flame dried flask (500mL), a solution of triphenylphosphine (17.18 g, 65.5 mmol) in dichloromethane (100 mL, SPS quality) was dropwise added during 30 minutes. The mixture was allowed to react 30 min at 0 ºC and a suspension of 4-hydroxybenzaldehyde (2.00 g, 16.38 mmol) in dichloromethane (30 mL) was dropwise added. After 2 h at 0 ºC methanol (10 mL) was added and the mixture was allowed to react for 30 min at rt. Finally the mixture was concentrated and the product was purified by column chromatography using a mixture of hexanes and ethyl acetate as eluent. The product was obtained as a white solid (2.97 g, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 5.38 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.54, 136.13, 130.09, 128.07, 115.27, 87.46.

ii) Synthesis of 4-ethynylphenol (**3**).



4-(2,2-dibromovinyl)phenol (2.94 g, 10.58 mmol) was dissolved in dry THF (SPS quality) in a flame dried flask and cooled to -78 ºC. A solution of *n*-butyllithium (2.5 M in hexanes) was then added via syringe (3.22 mL, 34.93 mmol). After 1 h the reaction was quenched with water (1 mL) and allowed to react for 30 min. The reaction was then treated with 20 mL of saturated solution of NH_4Cl and extracted with EtOAc (3 x 10 mL). The organic layer was dried with brine (10 mL) and over Na_2SO_4. The product was purified by column chromatography using a mixture of hexanes and ethyl acetate as eluent. The product was obtained as a white solid (582 mg, 81 %). ^{1}H NMR (400 MHz, MeOD) δ 7.28 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 3.24 (s, 1H). ^{13}C NMR (101 MHz, MeOD) δ 159.21, 134.48, 116.34, 114.43, 84.77, 76.29. IR (ATR): ν = 3380, 3284, 2104, 1607, 1586, 1506, 1219, 1167 cm^{-1}.

Synthesis of prop-2-ynyl 4-hydroxybenzoate (4).

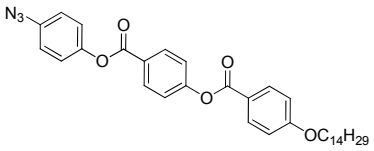


Sodium bicarbonate (2.43 g, 29.00 mmol) and 4-hydroxybenzoic acid (2.00 g, 14.48 mmol) were suspended in DMF (20 mL). The temperature was set to 80ºC under stirring for one hour. Then 3-bromoprop-1-yne (1.61 ml, 14.48 mmol) was added all at once. The mixture was allowed to react at 80ºC for 4h and allowed to slowly reach rt (converts into a suspension). After 16 h, the mixture was poured into aqueous solution $NaHCO_3$ (saturated (50 mL)) and extracted with diethyl ether (3x20 mL). The organic phases were combined and dried with brine (20mL) and Na_2SO_4. After filtration and removal of the solvent a yellow residue was obtained. the title product was obtained as a white crystalline solid (needles) after recrystallization from DCM/hexanes (1.54 g, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.58 (s, 1H), 4.90 (d, *J* = 2.3 Hz, 2H), 2.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.03, 160.63, 132.22, 121.45, 115.38, 77.76, 74.99, 52.37. IR (ATR): ν = 3330, 3255, 2959, 2123, 1692, 1604, 1591, 1436, 1274, 1257, 1165, 1095 cm^{-1}. HRMS: calcd for $C_{10}H_7O_3$ (M^+) 175.0395, found 175.0401.

Synthetic procedure for the azido-functionalized intermediates 9-14. [lateral structures of the bent-core compounds]

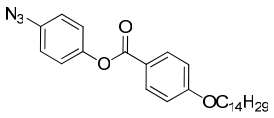
To a solution of **1** or **2** (1.00 to 1.66 equiv) in dichloromethane (SPS quality, 40 mL), the corresponding acid **5**-**8** (1 equiv) and DMAP (0.2 equiv) were added under argon atmosphere. The mixture was cooled in a water-ice bath and a solution of N,N'-dicyclohexylcarbodiimide (DCC) (1.2 equiv) in dichloromethane (5 mL) was added dropwise. The reaction mixture was stirred for 16h at room temperature. After this time, the white solid was filtered off and the solvent evaporated.

Synthesis of 4-azidophenyl 4-(4-tetradecyloxybenzoyloxy)benzoate (9).



The product was synthesized from **1** (134 mg, 0.99 mmol) and **5** (300 mg, 0,66 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. Subsequent recrystallization from a mixture of hexanes and dichloromethane yielded the title compound as a white solid (238 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 4.05 (t, *J* = 6.6 Hz, 1H), 3.49 (d, *J* = 4.7 Hz, 1H), 1.82 (dd, *J* = 14.6, 6.8 Hz, 1H), 1.53 – 1.17 (m, 11H), 0.88 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.44, 164.30, 163.84, 155.48, 147.79, 137.64, 132.41, 131.80, 126.59, 123.09, 122.14, 120.89, 119.93, 114.42, 68.40, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.08, 25.97, 22.68, 14.11. IR (ATR): ν = 2917, 2849, 2111, 1741, 1603, 1504, 1470, 1268, 1202 cm^{-1}. HRMS: calcd for $C_{34}H_{41}N_3O_5$ (MNa^+) 594.2944, found 594.2941.

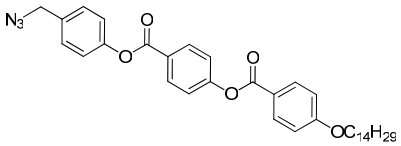
Synthesis of 4-azidophenyl 4-tetradecyloxybenzoate (10).



The product was synthesized from **1** (572 mg, 3.47 mmol) and **6** (700 mg, 2.09 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. Subsequent recrystallization from a mixture of hexanes and dichloromethane yielded the title compound as a white solid (708 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 1.93 – 1.73 (m, 2H), 1.58 – 1.07 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.88, 163.63, 148.00, 137.35, 132.26, 123.18, 121.20, 119.84, 114.31, 68.34, 55.74, 34.91, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.08, 25.97, 25.45, 24.69, 22.68, 14.11. IR (ATR): ν = 2916, 2848, 2107,

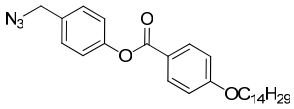
2075, 1724, 1607, 1504, 1472, 1287, 1256, 1206 cm^{-1}. HRMS: calcd for $C_{27}H_{37}N_3O_3$ (MNa^+) 474.2733, found 474.2743.

Synthesis of 4-(azidomethyl)phenyl 4-(4-tetradecyloxybenzoyloxy)benzoate (11).



The product was synthesized from **2** (100 mg, 0.67 mmol) and **5** (305 mg, 0.67 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. The title compound as a white solid (224 mg, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.32 (m, 4H), 7.24 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 4.38 (s, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.30 (d, *J* = 28.1 Hz, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.31, 163.84, 155.47, 150.81, 133.14, 132.41, 131.82, 129.35, 126.70, 122.15, 122.13, 120.92, 114.42, 68.40, 54.22, 34.93, 31.92, 29.65, 29.58, 29.55, 29.36, 29.08, 25.98, 22.69, 14.12. IR (ATR): ν = 3107, 2956, 2849, 2099, 1737, 1603, 1510, 1278, 1257 cm^{-1}. HRMS: calcd for $C_{35}H_{43}N_3O_5$ (MNa^+) 608.3100, found 608.3094.

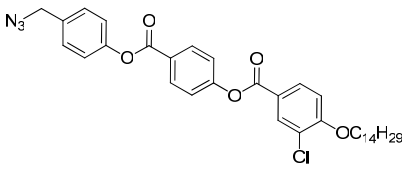
Synthesis of 4-(azidomethyl)phenyl 4-tetradecyloxybenzoate (12).



The product was synthesized from **2** (100 mg, 0.673 mmol) and **6** (150 mg, 0,45 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. Subsequent recrystallization from hexanes yielded the title compound as a white solid (115 mg, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.37 (s, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.73 (m, 2H), 1.37 (d, *J* = 84.0 Hz, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.13, 163.93, 151.32, 133.15, 132.60, 132.03, 129.60, 122.56, 121.64, 114.68, 114.63, 68.67, 54.57, 32.24, 30.00, 29.99, 29.97, 29.90, 29.87, 29.67, 29.41, 26.29,

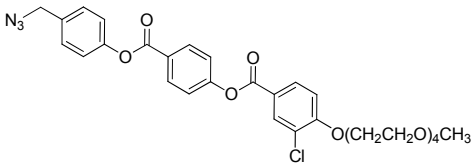
23.01, 14.43. IR (ATR): ν = 2916, 2849, 2171, 2113, 1726, 1607, 1510, 1470, 1284, 1251 cm^{-1}. HRMS: calcd for $C_{28}H_{39}N_3O_3$ (MNa^+) 488.2889, found 488.2906.

Synthesis of 4-(azidomethyl)phenyl 4-(3-chloro-4-tetradecyloxybenzoyloxy)benzoate (13).



The product was synthesized from **2** (128 mg, 0.86 mmol) and **7** (350 mg, 0.72 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. The title compound as a white solid (265 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 2.1 Hz, 1H), 8.08 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 4.38 (s, 2H), 4.14 (t, *J* = 6.5 Hz, 2H), 1.98 – 1.81 (m, 2H), 1.52 (m, 2H), 1.44 – 1.16 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.27, 163.38, 159.16, 155.16, 150.77, 133.17, 132.24, 131.86, 130.62, 129.35, 126.92, 123.18, 122.13, 122.02, 121.58, 112.23, 69.49, 54.21, 31.92, 29.67, 29.64, 29.56, 29.51, 29.35, 29.28, 28.88, 25.88, 22.68, 14.11. IR (ATR): ν = 2918, 2851, 2099, 1723, 1596, 1509, 1467, 1270, 1192, 1161 cm^{-1}. MS (TOF MS ES+): calcd for $C_{35}H_{42}N_3O_5Cl$ (MNa^+) 642.27, found 642.3.

Synthesis of 4-(azidomethyl)phenyl 4-(3-chloro-4-(2,5,8,11-tetraoxatridecan-13-yloxy)benzoyloxy)benzoate (14).



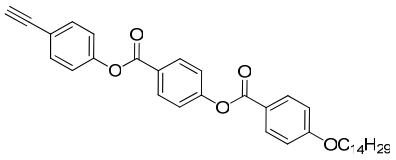
The product was synthesized from **2** (139 mg, 0.93 mmol) and **7** (300 mg, 0.62 mmol). Purification was performed by flash column chromatography using a mixture of ethyl acetate and methanol as eluent. The title compound was obtained as a white solid (276 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 2.1 Hz, 1H), 8.09 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.39 (t, *J* = 9.0 Hz, 4H), 7.26 (s, 3H), 7.06 (d, *J* = 8.7 Hz, 1H), 4.38 (s, 2H), 4.34 – 4.25 (m, 2H), 4.01 – 3.92 (m,

2H), 3.83 – 3.75 (m, 2H), 3.73 – 3.61 (m, 8H), 3.55 (m, 2H), 3.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.16, 132.29, 131.86, 130.58, 129.34, 126.95, 123.26, 122.12, 122.07, 122.00, 112.56, 71.93, 71.18, 70.69, 70.62, 70.52, 69.28, 69.15, 59.02, 54.19. IR (ATR): ν = 2873, 2096, 1730, 1597, 1511, 1453, 1280, 1163 cm^{-1}. HRMS: calcd for $C_{30}H_{32}N_3O_9Cl$ (MNa^+) 636.1725, found 636.1705.

Synthetic procedure for the ethyne-functionalized intermediates 15-18. [lateral structures of the bent-core compounds]

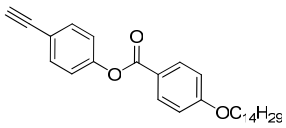
To a solution of **3** or **4** (1.00 to 2.50 equiv) in dichloromethane (SPS quality, 40 mL), the corresponding acid **5**-**6** (1 equiv) and DMAP (0.2 equiv) were added under argon atmosphere. The mixture was cooled in a water-ice bath and a solution of N,N'-dicyclohexylcarbodiimide (DCC) (1.2 equiv) in dichloromethane (5 mL) was added dropwise. The reaction mixture was stirred for 16h at room temperature. After this time, the white solid was filtered off and the solvent evaporated.

Synthesis of 4-ethynylphenyl 4-(4-tetradecyloxybenzoyloxy)benzoate (15)



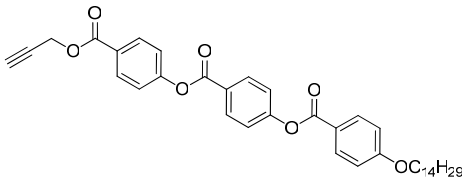
The product was synthesized from **3** (275 mg, 2.33 mmol) and **5** (400 mg, 0.88 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. Subsequent recrystallization from a mixture of hexanes and dichloromethane yielded the title compound as a white solid (488 mg, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.08 (s, 1H), 1.89 – 1.77 (m, 2H), 1.52 – 1.43 (m, 2H), 1.43 – 1.18 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.27, 164.09, 163.83, 155.50, 151.09, 133.39, 132.40, 131.82, 126.53, 122.14, 121.83, 120.88, 119.86, 114.41, 82.84, 77.35, 68.38, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.07, 25.96, 22.68, 14.11. IR (ATR): ν = 3283, 2917, 2848, 1741, 1727, 1602, 1509, 1470, 1255, 1201, 1191, 1159 cm^{-1}. HRMS: calcd for $C_{36}H_{42}O_5$ (MNa^+) 577.2930, found 577.2920.

Synthesis of 4-ethynylphenyl 4-tetradecyloxybenzoate (16).



The product was synthesized from **3** (250 mg, 2.12 mmol) and **6** (300 mg, 0.90 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. Subsequent recrystallization from a mixture of hexanes and dichloromethane yielded the title compound as a white solid (342 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 3.07 (s, 1H), 1.89 – 1.75 (m, 2H), 1.37 (d, *J* = 82.8 Hz, 22H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.55, 163.67, 151.34, 133.32, 132.31, 121.93, 121.18, 119.57, 114.34, 82.96, 77.19, 68.35, 31.92, 29.68, 29.67, 29.65, 29.58, 29.55, 29.35, 29.08, 25.97, 22.69, 14.11. IR (ATR): ν = 3281, 2917, 2848, 1726, 1605, 1509, 1471, 1256, 1203, 1165 cm^{-1}. HRMS: calcd for $C_{29}H_{38}O_3$ (MNa^+) 457.2719, found 457.2716.

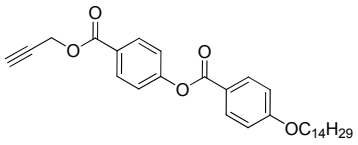
Synthesis of prop-2-ynyl 4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoate (17).



The product was synthesized from **4** (106 mg, 0.60 mmol) and **5** (260 mg, 0.57 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. The title compound was obtained as a white solid (298 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 2H), 8.22 – 8.08 (m, 4H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.94 (d, *J* = 2.3 Hz, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 2.53 (t, *J* = 2.3 Hz, 1H), 1.92 – 1.75 (m, 2H), 1.54 – 1.13 (m, 22H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.00, 164.26, 163.85, 155.62, 154.87, 132.41, 131.87, 131.49, 127.04, 126.33, 122.20, 121.86, 120.85, 114.42, 77.61, 75.09, 68.39, 52.56, 31.91, 29.67, 29.66, 29.64, 29.57, 29.54, 29.34, 29.07, 25.96, 22.68, 14.10.

IR (ATR): ν = 3310, 2935, 2848, 1734, 1600, 1509, 1279, 1257 cm^{-1}. HRMS: calcd for $C_{38}H_{44}O_7$ (MNa^+) 635.2985, found 635.2986.

Synthesis of prop-2-ynyl 4-(4-tetradecyloxybenzoyloxy)benzoate (18).

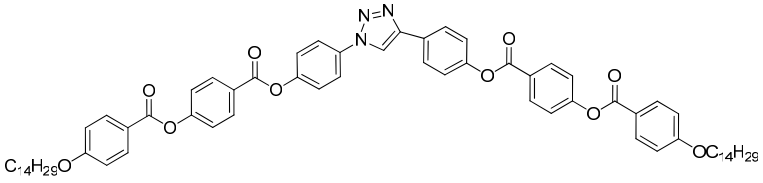


The product was synthesized from **4** (137 mg, 0.78 mmol) and **6** (247 mg, 0.74 mmol). Purification was performed by flash column chromatography using a mixture of hexanes and dichloromethane as eluent. The title compound was obtained as a white solid (271 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.06 (m, 4H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.93 (d, *J* = 2.4 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 2.53 (t, *J* = 2.3 Hz, 1H), 1.95 – 1.70 (m, 2H), 1.55 – 1.13 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.06, 164.27, 163.77, 155.14, 132.35, 131.39, 126.73, 121.92, 120.94, 114.37, 77.64, 75.05, 68.36, 52.51, 31.90, 29.67, 29.65, 29.63, 29.56, 29.53, 29.33, 29.06, 25.95, 22.67, 14.09. IR (ATR): ν = 3282, 2915, 2848, 2131, 1729, 1603, 1508, 1470, 1271, 1251, 1095 cm^{-1}. HRMS: calcd for $C_{31}H_{40}O_5$ (MNa^+) 515.2773, found 515.2773.

Synthetic procedure for T, M and MC series.

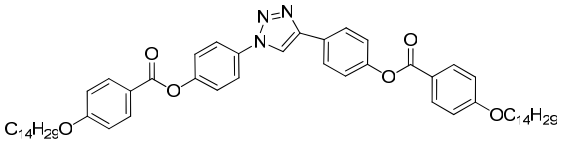
Catalyst **I** (2 mol%) was added to a solution of azido-functionalized compound **9**-**14** (0.06 mmol) and the appropriate alkyne-functionalized compound compound **15**-**18** in 2 mL THF/DMF mixture (1/1 ratio) in a microwave reaction tube. The reaction was run for 1 h under microwave irradiation (T_{max} = 80 ºC). After that time, the reaction product had appeared as a white precipitate.

Synthesis of 1-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-1*H*-1,2,3-triazol (T1).



The synthesis was performed following the general procedure with **9** (41 mg, 0.07 mmol) and **15** (40 mg, 0.07 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (58 mg, 71 %). ^{1}H NMR (400 MHz, Toluene-d8) δ 8.22 – 8.08 (m, 8H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.39 (s, 1H), 7.27 (d, *J* = 8.7 Hz, 4H), 7.24 – 7.18 (m, 4H), 6.83 – 6.77 (m, 4H), 3.73 (t, *J* = 6.4 Hz, 4H), 1.71 – 1.59 (m, 4H), 1.45 – 1.12 (m, 44H), 0.98 – 0.82 (m, 6H). ^{13}C NMR (126 MHz, Toluene-d8, 373K) δ 163.93, 163.84, 163.79, 163.62, 151.74, 151.32, 147.65, 137.59, 137.56, 137.50, 137.45, 137.40, 137.30, 137.10, 134.69, 132.18, 132.13, 129.19, 129.16, 129.13, 129.07, 129.02, 128.98, 128.80, 128.57, 128.379, 128.19, 128.01, 127.94, 127.68, 127.49, 127.29, 126.82, 124.84, 124.65, 124.46, 122.65, 122.05, 121.12, 116.96, 114.55, 114.46, 68.28, 68.22, 31.84, 29.64, 29.61, 29.55, 29.51, 29.30, 29.26, 29.16, 25.97, 22.51, 20.23, 20.08, 19.93, 19.77, 19.62, 19.47, 19.32, 13.56. IR (ATR): ν = 2916, 2849, 1737, 1605, 1511, 1282, 1256 cm^{-1}. HRMS (MALDI+): calcd for $C_{70}H_{83}N_3O_{10}$ (MH^+) 1126.6151, found 1126.6107.

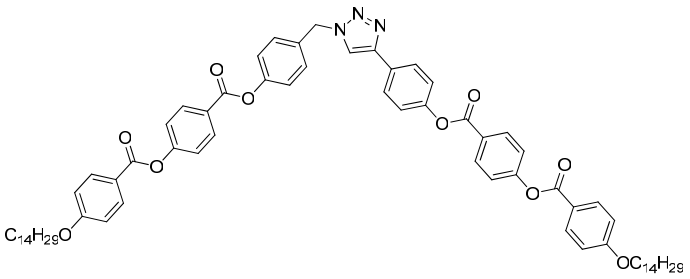
Synthesis of 1-(4-(4-tetradecyloxybenzoyloxy)phenyl)-4-(4-(4-tetradecyloxybenzoyloxy)phenyl)-1*H*-1,2,3-triazol (T2).



The synthesis was performed following the general procedure with **10** (42 mg, 0.09 mmol) and **16** (40 mg, 0.09 mmol) in the presence of catalyst **I** (1.1 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high

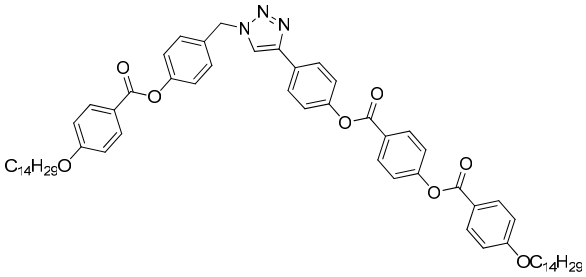
vacuum. The title product was obtained as a white solid (61 mg, 75 %). ^{1}H NMR (500 MHz, Toluene-d8, 373K) δ 8.16 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 8.7 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.39 (s, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.86 – 6.71 (m, 4H), 3.74 (t, *J* = 6.5 Hz, 4H), 1.78 – 1.58 (m, 4H), 1.53 – 1.08 (m, 44H), 0.99 – 0.76 (m, 6H). ^{13}C NMR (126 MHz, Toluene-D8, 373K) δ 164.70, 164.59, 164.57, 164.34, 152.48, 152.03, 152.00, 148.39, 135.45, 132.96, 132.92, 129.46, 128.55, 127.57, 125.72, 123.44, 123.31, 122.86, 122.77, 121.87, 117.65, 115.27, 115.18, 68.98, 68.92, 32.65, 30.45, 30.43, 30.36, 30.31, 30.08, 29.90, 26.74, 23.33, 14.39. IR (ATR): ν = 2917, 2849, 1726, 1608, 1511, 1472, 1294, 1254 cm^{-1}. HRMS (MALDI+): calcd for $C_{56}H_{75}N_3O_6$ (MH^+) 886.5729, found 886.5818.

Synthesis of 1-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-1*H*-1,2,3-triazol (M1).



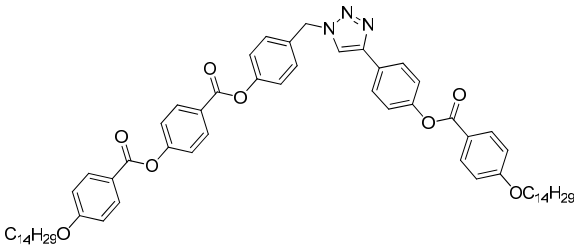
The synthesis was performed following the general procedure with **11** (42 mg, 0.07 mmol) and **15** (40 mg, 0.07 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (55 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 – 8.21 (m, 4H), 8.14 (d, *J* = 7.9 Hz, 4H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.69 (s, 1H), 7.45 – 7.33 (m, 6H), 7.33 – 7.26 (m, 4H), 6.98 (d, *J* = 8.7 Hz, 4H), 5.61 (s, 2H), 4.06 (t, *J* = 6.5 Hz, 4H), 1.95 – 1.70 (m, 4H), 1.54 – 1.06 (m, 60H), 0.88 (t, *J* = 6.6 Hz, 7H). IR (ATR): ν = 2916, 2849, 1726, 1604, 1510, 1470, 1284, 1254 cm^{-1}. HRMS (MALDI+): calcd for $C_{71}H_{85}N_3O_{10}$ (MNa^+) 1162.6127, found 1162.6253.

Synthesis of 1-(4-(4-tetradecyloxybenzoyloxy)phenylmethyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-1*H*-1,2,3-triazol (M2).



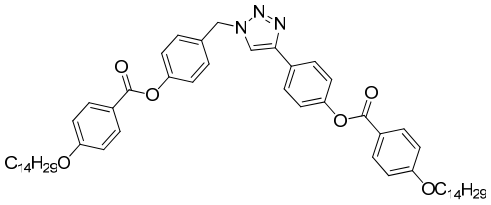
The synthesis was performed following the general procedure with **12** (34 mg, 0.07 mmol) and **15** (40 mg, 0.07 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (41 mg, 56 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.67 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 4H), 7.33 – 7.25 (m, 4H), 7.09 – 6.82 (m, 4H), 5.59 (s, 2H), 4.21 – 3.92 (m, 4H), 2.02 – 1.71 (m, 4H), 1.67 – 1.06 (m, 44H), 0.88 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 328K) δ 174.47, 164.68, 164.32, 164.27, 163.98, 163.85, 157.73, 155.61, 151.70, 147.74, 132.43, 132.34, 132.04, 131.80, 129.26, 128.55, 127.02, 126.98, 122.68, 122.11, 122.07, 121.48, 121.28, 119.43, 114.59, 114.53, 68.52, 53.78, 31.94, 29.67, 29.65, 29.59, 29.56, 29.36, 29.34, 29.17, 26.03, 22.67, 14.01. IR (ATR): ν = 2917, 2850, 1726, 1606, 1511, 1470, 1416, 1290, 1254, 1208, 1163 cm^{-1}. HRMS (MALDI+): calcd for $C_{64}H_{81}N_3O_8$ (MNa^+) 1042.5916, found 1042.6049.

Synthesis of 1-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-tetradecyloxybenzoyloxy)phenyl)-1*H*-1,2,3-triazol (M3).



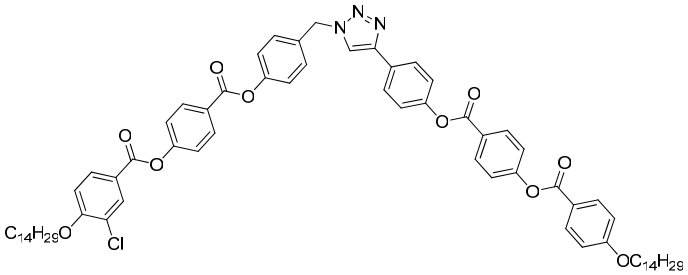
The synthesis was performed following the general procedure with **11** (40 mg, 0.07 mmol) and **16** (30 mg, 0.07 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (45 mg, 65 %). ^{1}H NMR (500 MHz, $CDCl_3$, 328K) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.20 – 8.10 (m, 4H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.67 (s, 1H), 6.98 (d, *J* = 6.7 Hz, 2H), 6.96 (d, *J* = 6.7 Hz, 2H), 5.60 (s, 2H), 4.15 – 3.96 (m, 4H), 1.87 – 1.77 (m, 4H), 1.62 – 1.21 (m, 44H), 0.88 (t, *J* = 6.8 Hz, 6H). IR (ATR): ν = 2916, 2849, 1725, 1605, 1509, 1470, 1288, 1252 cm^{-1}. HRMS (MALDI+): calcd for $C_{64}H_{81}N_3O_8$ (MNa^+) 1042.5916, found 1042.5918.

Synthesis of 1-(4-(4-tetradecyloxybenzoyloxy)phenylmethyl)-4-(4-(4-tetradecyloxybenzoyloxy)phenyl)-1*H*-1,2,3-triazol (M4).



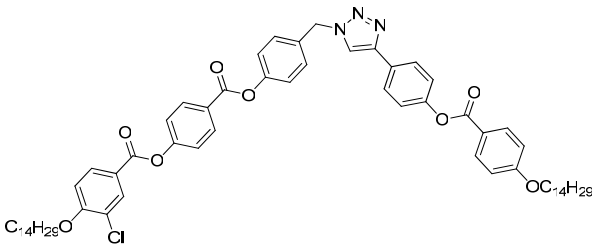
The synthesis was performed following the general procedure with **12** (42 mg, 0.07 mmol) and **16** (40 mg, 0.07 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (55 mg, 67 %). ^{1}H NMR (500 MHz, Toluene-d8, 373K) δ 8.13 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.10 – 7.07 (m, 2H), 7.02 (s, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 6.3 Hz, 2H), 6.75 (d, *J* = 6.3 Hz, 2H), 4.97 (s, 2H), 3.72 (dd, *J* = 12.1, 6.4 Hz, 4H), 1.68 – 1.57 (m, 4H), 1.33 (d, *J* = 24.3 Hz, 44H), 0.94 – 0.83 (m, 6H). IR (ATR): ν = 2916, 2849, 1726, 1606, 1510, 1470, 1283, 1254, 1165 cm^{-1}. HRMS (MALDI+): calcd for $C_{57}H_{77}N_3O_6$ (MH^+) 900.5885, found 900.6093.

Synthesis of 1-(4-(4-(3-chloro-4-tetradecyloxybenzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-1*H*-1,2,3-triazol (M5).



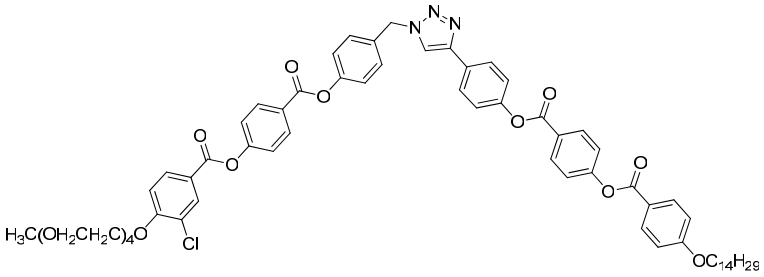
The synthesis was performed following the general procedure with **13** (35 mg, 0.06 mmol) and **15** (31 mg, 0.06 mmol) in the presence of catalyst **I** (0.7 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (54 mg, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.7, 2.7 Hz, 4H), 8.22 (d, *J* = 2.1 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 2H), 8.08 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 4H), 7.33 – 7.26 (m, 4H), 7.06 – 6.94 (m, 3H), 5.63 (s, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.86 – 1.76 (m, 2H), 1.52 – 1.16 (m, 44H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 328K) δ 164.33, 164.18, 163.99, 163.33, 159.37, 155.63, 155.46, 151.47, 151.05, 147.79, 132.44, 132.37, 131.89, 131.81, 130.60, 129.33, 128.54, 127.00, 123.56, 122.58, 122.22, 122.13, 122.08, 122.04, 121.93, 121.29, 119.44, 114.60, 112.53, 69.70, 68.56, 53.74, 31.94, 29.69, 29.67, 29.65, 29.59, 29.56, 29.52, 29.36, 29.34, 29.29, 29.17, 28.99, 26.02, 25.94, 22.66, 14.00. IR (ATR): ν = 2915, 2849, 1729, 1598, 1509, 1470, 1274, 1202, 1168 cm^{-1}. HRMS: calcd for $C_{71}H_{84}N_3O_{10}Cl$ (MH^+) 1174.5918, found 1174.5979.

Synthesis of 1-(4-(4-(3-chloro-4-tetradecyloxybenzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-tetradecyloxybenzoyloxy)phenyl)-1*H*-1,2,3-triazol (M6).



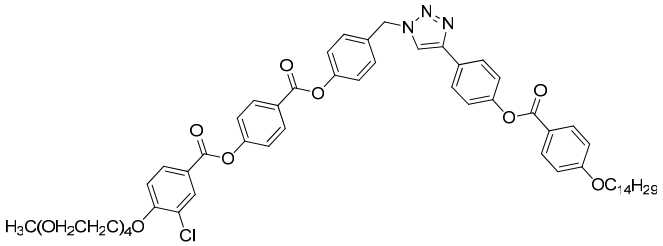
The synthesis was performed following the general procedure with **13** (40 mg, 0.06 mmol) and **16** (28 mg, 0.06 mmol) in the presence of catalyst **I** (0.7 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The title product was obtained as a white solid (42 mg, 64 %).^{1}H NMR (500 MHz, $CDCl_3$, 323K) δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 2.1 Hz, 1H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.07 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.68 (s, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 5.60 (s, 2H), 4.13 (t, *J* = 6.5 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 1.89 (dd, *J* = 14.3, 7.3 Hz, 2H), 1.81 (dd, *J* = 14.7, 6.8 Hz, 2H), 1.42 – 1.10 (m, 44H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, 323K) δ 164.33, 164.27, 164.20, 164.18, 163.99, 163.33, 159.37, 155.63, 155.46, 151.47, 151.05, 147.79, 132.44, 132.42, 132.37, 132.31, 131.89, 131.81, 130.60, 129.33, 128.54, 127.00, 123.56, 122.58, 122.22, 122.13, 122.08, 122.04, 121.93, 121.29, 119.44, 114.60, 112.53, 69.70, 68.56, 53.74, 31.94, 29.69, 29.67, 29.65, 29.59, 29.56, 29.56, 29.52, 29.36, 29.34, 29.29, 29.17, 28.99, 26.02, 25.94, 22.66, 14.00. IR (ATR): ν = 2917, 2850, 1728, 1607, 1469, 1291, 1254 cm^{-1}. HRMS: calcd for $C_{64}H_{80}N_3O_8Cl$ (MH^+) 1054.5707, found 1054.5679.

Synthesis of 1-(4-(4-(3-chloro-4-(2,5,8,11-tetraoxatridecan-13-yloxy)benzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-1*H*-1,2,3-triazol (M7).



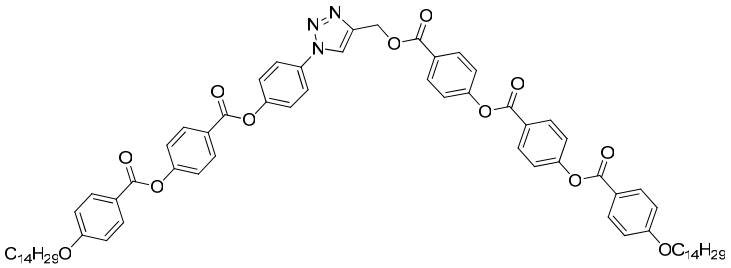
The synthesis was performed following the general procedure with **14** (36 mg, 0.06 mmol) and **15** (32 mg, 0.06 mmol) in the presence of catalyst **I** (0.7 mg, 0.02 equiv). When the reaction was complete, the mixture was concentrated and filtered. The white solid was then washed with water (3 x 2 mL) and dried under high vacuum. The product was dissolved in a minimum amount of chloroform and precipitated by addition to ethyl acetate. The suspension was centrifuged and the solid was washed with hexanes. The title product was obtained as a white solid (35 mg, 53 %). ^{1}H NMR (400 MHz, CDCl3) δ 8.33 – 8.25 (m, 4H), 8.23 (d, J = 2.1 Hz, 1H), 8.15 (d, J = 8.9 Hz, 2H), 8.09 (dd, J = 8.7, 2.1 Hz, 1H), 7.89 (d, J = 8.7 Hz, 2H), 7.72 (s, 1H), 7.41 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.7 Hz, 4H), 7.32 – 7.27 (m, 4H), 7.05 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 8.9 Hz, 2H), 5.63 (s, 2H), 4.33 – 4.27 (m, 2H), 4.05 (t, J = 6.6 Hz, 2H), 3.99 – 3.94 (m, 2H), 3.82 – 3.76 (m, 2H), 3.71 – 3.63 (m, 8H), 3.58 – 3.51 (m, 2H), 3.38 (s, 4H), 1.87 – 1.78 (m, 2H), 1.53 – 1.42 (m, 2H), 1.42 – 1.20 (m, 20H), 0.88 (t, J = 6.8 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 164.30, 164.20, 163.28, 155.41, 151.18, 150.78, 132.40, 132.30, 131.89, 131.80, 130.59, 129.32, 128.34, 126.89, 126.78, 123.27, 122.55, 122.14, 122.10, 122.04, 120.92, 114.41, 112.57, 71.93, 71.17, 70.68, 70.62, 70.52, 69.28, 69.15, 68.39, 59.02, 31.91, 29.64, 29.57, 29.54, 29.34, 29.07, 25.96, 22.68, 14.11. IR (ATR): ν = 2918, 2850, 1732, 1599, 1510, 1461, 1259, 1201, 1161 cm^{-1}. HRMS: calcd for $C_{66}H_{74}N_3O_{14}Cl$ (MNa^+) 1190.4757, found 1190.4755.

Synthesis of 1-(4-(4-(3-chloro-4-(2,5,8,11-tetraoxatridecan-13-yloxy)benzoyloxy)benzoyloxy)phenylmethyl)-4-(4-(4-tetradecyloxybenzoyloxy)phenyl)-1*H*-1,2,3-triazol (M8).



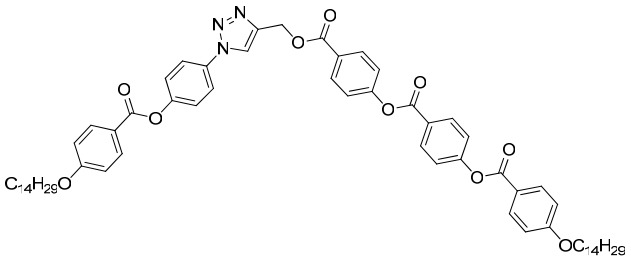
The synthesis was performed following the general procedure with **14** (40 mg, 0.07 mmol) and **16** (28 mg, 0.07 mmol) in the presence of catalyst **I** (0.7 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) and the reaction mixture was filtered. The solid was then washed with water (3 x 2 mL) and dried under high vacuum. The product was dissolved in a minimum amount of chloroform and precipitated by addition to ethyl acetate. The suspension was centrifuged and the solid was washed with hexanes. The title product was obtained as a white solid (36 mg, 53 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 8.09 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.71 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.32 – 7.26 (m, 4H), 7.05 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.62 (s, 2H), 4.30 (t, *J* = 4.8 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 4.01 – 3.90 (m, 2H), 3.85 – 3.76 (m, 2H), 3.73 – 3.60 (m, 8H), 3.59 – 3.46 (m, 2H), 3.38 (s, 3H), 1.89 – 1.76 (m, 2H), 1.47 (d, *J* = 7.7 Hz, 2H), 1.42 – 1.15 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.86, 164.23, 163.61, 163.32, 158.96, 155.23, 151.20, 151.03, 147.77, 132.33, 132.31, 131.93, 130.63, 129.35, 128.10, 126.85, 123.31, 122.58, 122.27, 122.08, 121.44, 119.47, 114.33, 112.60, 77.23, 71.97, 71.22, 70.73, 70.66, 70.56, 69.32, 69.19, 68.37, 59.07, 53.69, 31.95, 29.71, 29.70, 29.68, 29.61, 29.58, 29.38, 29.12, 26.01, 22.72, 14.15. IR (ATR): ν = 2917, 2850, 1726, 1597, 1509, 1279, 1253 cm^{-1}. HRMS: calcd for $C_{59}H_{70}N_3O_{12}Cl$ (MNa^+) 1070.4546, found 1070.4552.

Synthesis of 1-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxymethyl)-1*H*-1,2,3-triazol (MC1).



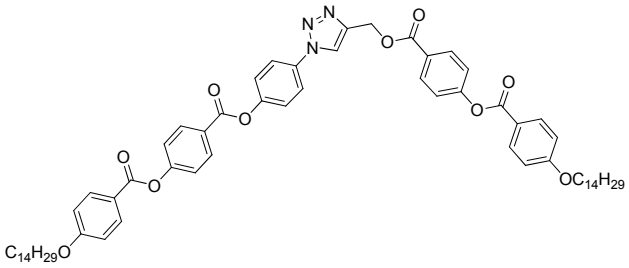
The synthesis was performed following the general procedure with **9** (38 mg, 0.06 mmol) and **17** (35 mg, 0.06 mmol) in the presence of catalyst **I** (0.7 mg, 0.02 equiv). When the reaction was complete, methanol was added (6 mL) to favor the precipitation of the product and the reaction mixture was filtered. The solid was then washed with methanol (5 mL) and with diethyl ether (2 x 5 mL), and dried under high vacuum. The title product was obtained as a white solid (59 mg, 81 %). 1H NMR (400 MHz, Toluene-d8) δ 8.17 – 7.96 (m, 10H), 7.52 (s, 1H), 7.34 (d, *J* = 8.9 Hz, 2H), 7.24 – 7.07 (m, 8H), 6.84 – 6.73 (m, 4H), 5.44 (s, 2H), 3.87 – 3.61 (m, 4H), 1.80 – 1.49 (m, 4H), 1.45 – 1.07 (m, 44H), 1.00 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, Toluene-d8, 373K) δ 165.88, 164.53, 164.50, 164.05, 163.99, 163.70, 156.61, 156.55, 155.82, 151.74, 135.36, 132.84, 132.09, 131.78, 127.60, 127.42, 127.39, 123.18, 122.54, 122.50, 122.43, 122.15, 121.83, 115.18, 115.17, 68.91, 58.71, 32.47, 30.27, 30.24, 30.17, 30.12, 29.91, 29.89, 29.75, 26.57, 23.14, 14.18. IR (ATR): ν = 2916, 2849, 1736, 1602, 1510, 1472, 1278, 1256, 1205, 1164 cm^{-1}. HRMS (MALDI+): calcd for $C_{72}H_{85}N_3O_{12}$ (MNa^+) 1206.6025, found 1206.6025.

Synthesis of 1-(4-(4-tetradecyloxybenzoyloxy)phenyl)-4-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)benzoyloxymethyl)-1*H*-1,2,3-triazol (MC2).



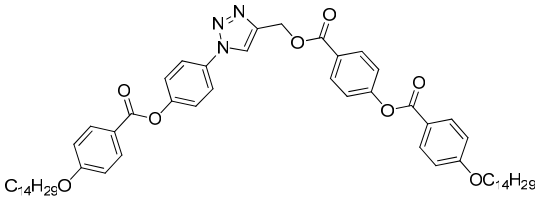
The synthesis was performed following the general procedure with **10** (30 mg, 0.07 mmol) and **17** (41 mg, 0.07 mmol) in the presence of catalyst **I** (0.8 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) to favor the precipitation of the product and the reaction mixture was filtered. The solid was then washed with water (2 x 2 mL), methanol (2 x 2 mL) and with diethyl ether (2 x 3 mL), and dried under high vacuum. The title product was obtained as a white solid (55 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 2H), 8.22 – 8.03 (m, 7H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 4H), 5.59 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 4H), 1.95 – 1.71 (m, 4H), 1.58 – 1.01 (m, 44H), 0.88 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 164.56, 164.26, 163.85, 163.81, 155.61, 154.84, 151.29, 134.32, 132.41, 132.38, 131.87, 131.48, 127.30, 126.34, 123.27, 122.19, 121.85, 121.80, 120.89, 120.86, 114.41, 77.20, 68.39, 58.12, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.07, 25.97, 22.68, 14.11. IR (ATR): ν = 2917, 2850, 1730, 1604, 1510, 1470, 1284, 1251 cm^{-1}. HRMS (MALDI+): calcd for $C_{65}H_{81}N_3O_{10}$ (MH^+) 1064.5995, found 1064.6137.

Synthesis of 1-(4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxy)phenyl)-4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxymethyl)-1*H*-1,2,3-triazol (MC3).



The synthesis was performed following the general procedure with **9** (44 mg, 0.08 mmol) and **18** (38 mg, 0.08 mmol) in the presence of catalyst **I** (0.9 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) to favor the precipitation of the product and the reaction mixture was filtered. The solid was then washed with water (2 x 2 mL), methanol (2 x 2 mL) and with diethyl ether (2 x 3 mL), and dried under high vacuum. The title product was obtained as a white solid (60 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 2H), 8.21 – 8.05 (m, 7H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.04 – 6.91 (m, 4H), 5.58 (s, 2H), 4.15 – 3.94 (m, 4H), 2.00 – 1.69 (m, 4H), 1.53 – 1.07 (m, 44H), 0.98 – 0.76 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 164.30, 164.27, 164.11, 163.86, 163.77, 155.65, 155.11, 151.02, 134.55, 132.42, 132.37, 131.88, 131.39, 127.01, 126.28, 123.19, 122.23, 121.93, 121.86, 120.96, 120.85, 114.43, 114.38, 77.20, 68.40, 68.37, 58.09, 31.91, 29.68, 29.66, 29.64, 29.58, 29.54, 29.35, 29.07, 25.97, 22.68, 14.11. IR (ATR): ν = 2917, 2849, 1731, 1604, 1510, 1470, 1279, 1253, 1205, 1163 cm^{-1}. HRMS (MALDI+): calcd for $C_{65}H_{81}N_3O_{10}$ (MH^+) 1064.5995, found 1064.5821.

Synthesis of 1-(4-(4-tetradecyloxybenzoyloxy)phenyl)-4-(4-(4-tetradecyloxybenzoyloxy)benzoyloxymethyl)-1*H*-1,2,3-triazol (MC4).



The synthesis was performed following the general procedure with **10** (41 mg, 0.09 mmol) and **18** (45 mg, 0.09 mmol) in the presence of catalyst **I** (1.1 mg, 0.02 equiv). When the reaction was complete, water was added (6 mL) to favor the precipitation of the product and the reaction mixture was filtered. The solid was then washed with water (2 x 2 mL), methanol (2 x 2 mL) and with diethyl ether (2 x 3 mL), and dried under high vacuum. The title product was obtained as a white solid (62 mg, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.05 (m, 6H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 6.2 Hz, 2H), 6.97 (d, *J* = 6.2 Hz, 2H), 5.58 (s, 2H), 4.32 – 3.75 (m, 4H), 1.95 – 1.72 (m, 4H), 1.53 – 1.07 (m, 44H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.79, 164.56, 164.30, 163.82, 163.78, 155.11, 151.28, 134.31, 132.38, 131.40, 127.02, 123.26, 121.93, 121.80, 120.97, 120.90, 114.41, 114.38, 77.20, 68.39, 58.10, 31.92, 29.68, 29.65, 29.58, 29.55, 29.35, 29.08, 25.97, 22.69, 14.11. IR (ATR): ν = 2917, 2849, 1726, 1605, 1511, 1464, 1280, 1252 cm^{-1}. HRMS: calcd for $C_{58}H_{77}N_3O_8$ (MNa^+) 966.5608, found 966.5589.

3. Textures of the intermediate compounds

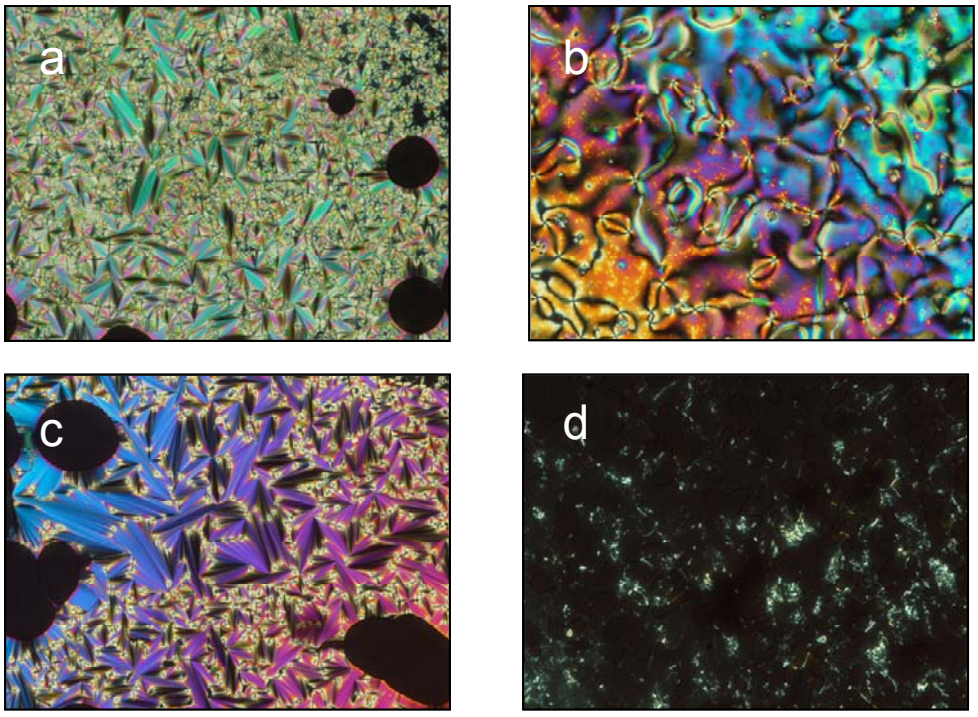


Figure S1. *Microphotographs of the textures of a) the SmA mesophase of compound* ***13*** *at 130ºC, b) the nematic mesophase of* ***16*** *at 81ºC, c) the SmA mesophase of* ***11*** *at 144ºC on cooling from the isotropic liquid and, d) the same as c) after shearing.*

4. DSC thermograms of representative bent-core compounds.

Figure S2. *DSC thermogram of the second heating and cooling scans at 10ºC/min of compound* ***M3.***

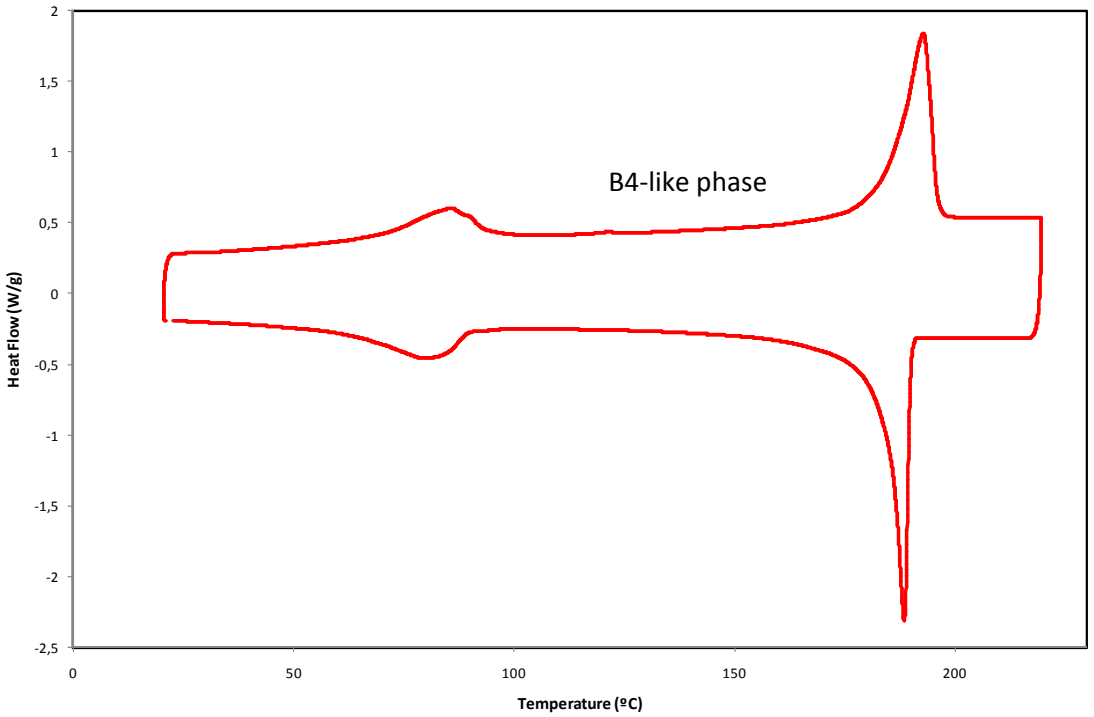


Figure S3*. DSC thermogram of the second heating and cooling scans at 10ºC/min of compound* ***M6.***

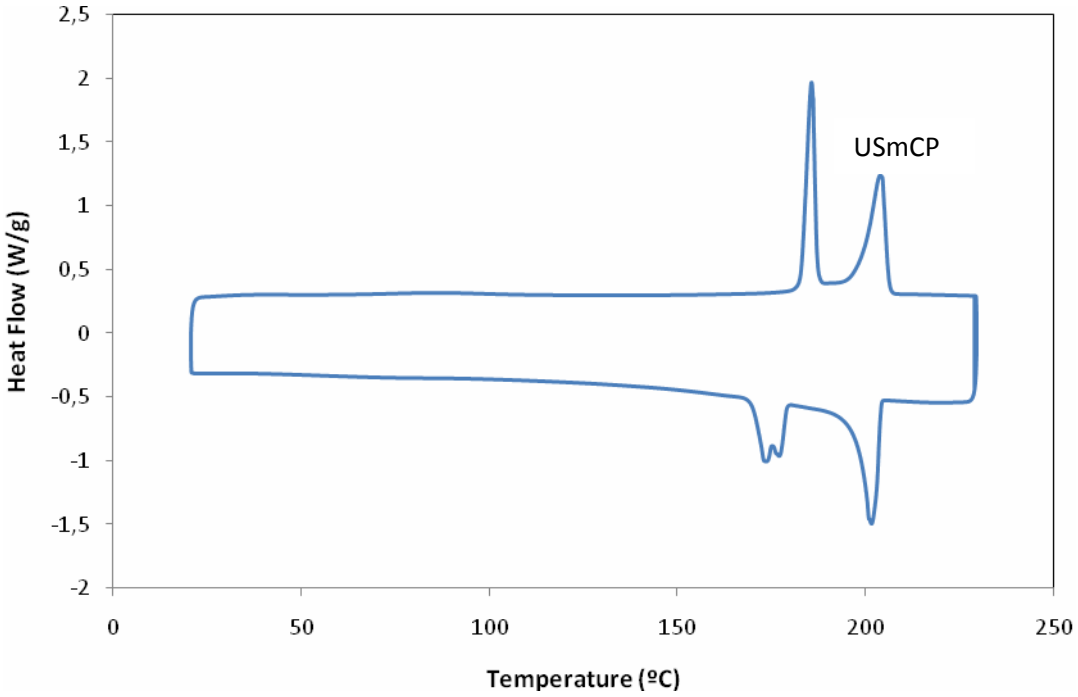
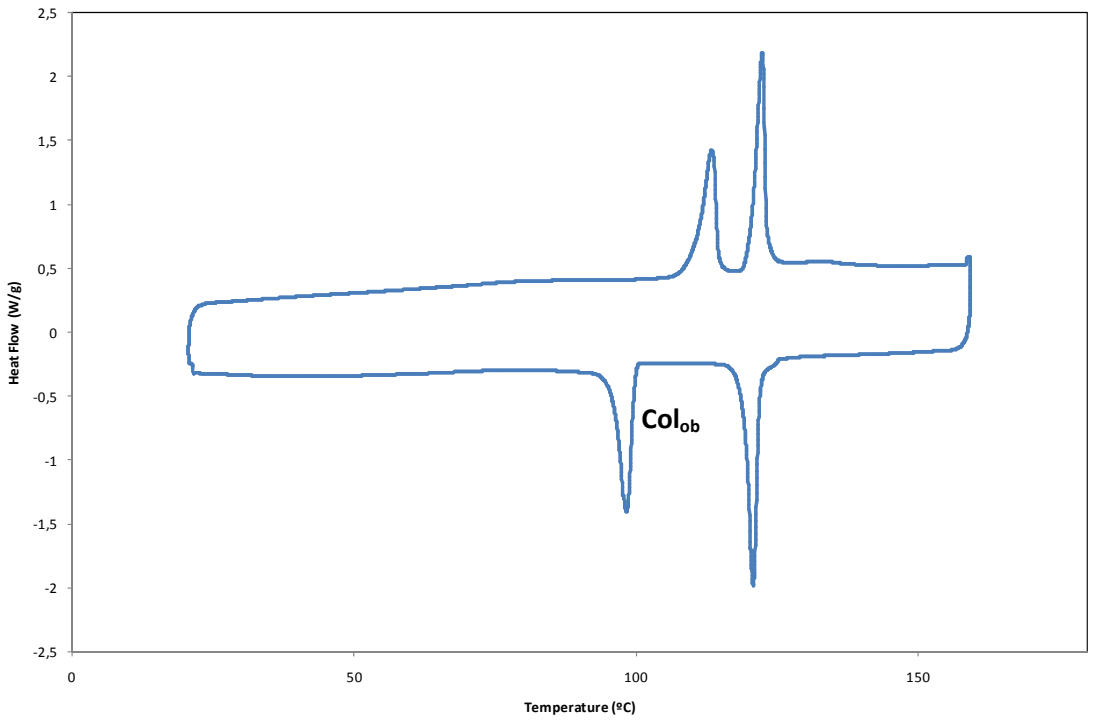


Figure S4. *DSC thermogram of the second heating and cooling scans at 10ºC/min of compound* ***MC4.***



[1] Gimeno, N.; Ros, M. B.; Serrano, J. L.; De la Fuente, M. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 5235.
[2] a) Loubinoux, B.; Miazimbakana, J.; Gerardin, P. *Tetrahedron Lett.* **1989**, *30*, 1939-1942. b) Q. Zhang, J. M. Takacs *Org. Lett.* **2008**, *10*, 545-548.